THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 44, PART 3 May 1, 1932 No. 243

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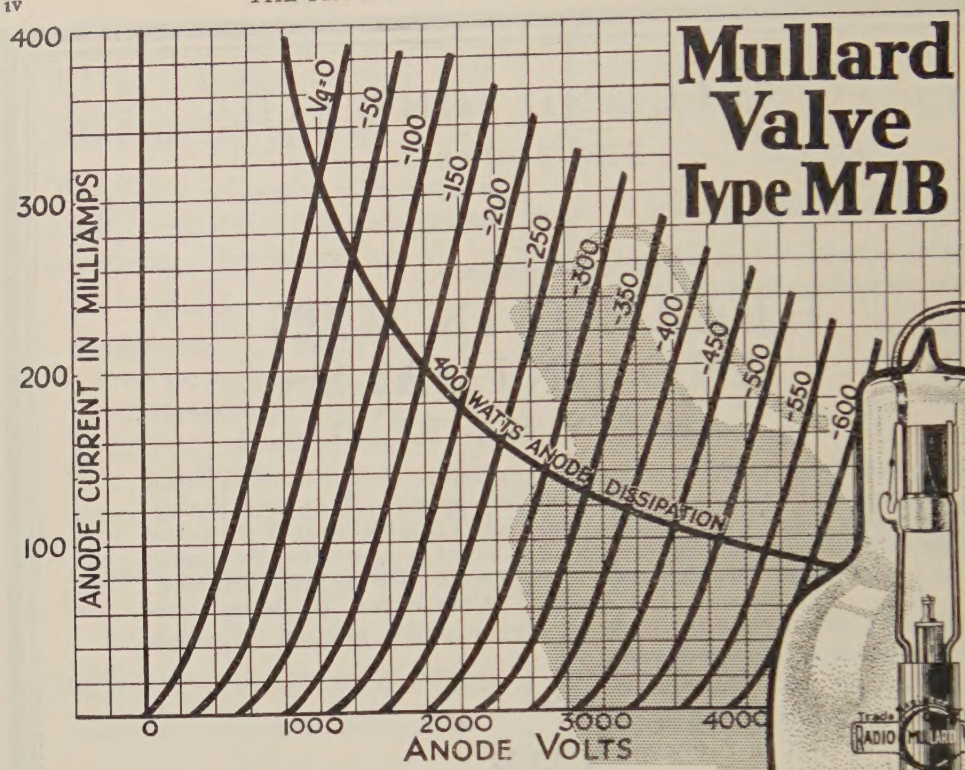

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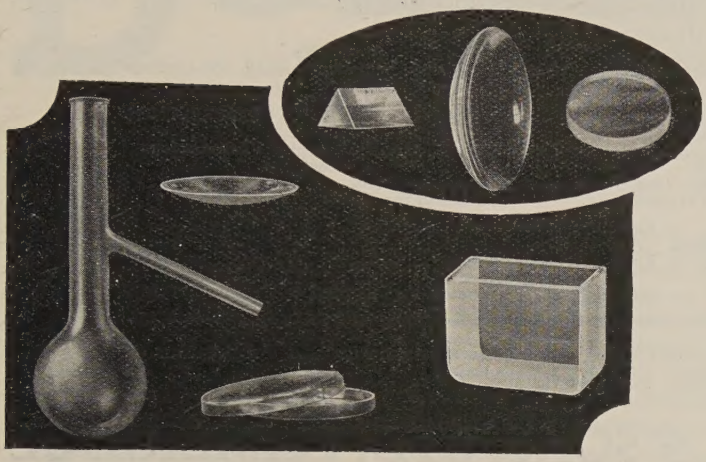

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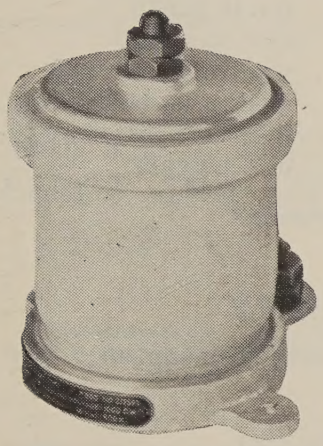

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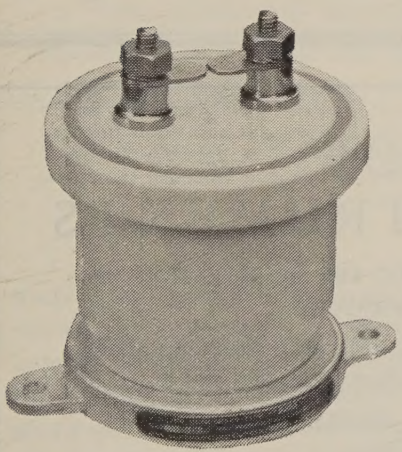

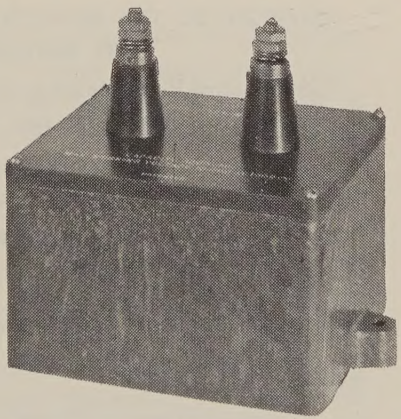

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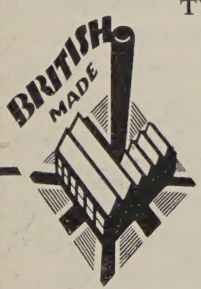

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ADDENDA

The following notes should be added:

Note 1. In figure 3 the lines represent the loci of intersection of the leaves. The vertical lines are traced by varying the voltage, the capacity being left constant; and the more or less horizontal curves are traced when the voltage is kept constant while the capacity is varied.

Note 2. Since the paper was written a case has been noted in which a spark discharge in one condenser left a charge in the leaf system, causing erratic readings for a time. It may be pointed out that this can only occur when the insulation of the condensers and leaf system is exceedingly high, and need cause no trouble in practice; there is sufficient leak in a ballast condenser insulated with the best bakelite to dissipate such a charge instantly.

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VOL. 44, PART 3 *May* 1, 1932 NO. 243

THE RAPID DETERMINATION OF MOISTURE IN SEEDS AND OTHER GRANULAR SUBSTANCES

BY R. M. DAVIES, M.Sc., University College of Wales, Aberystwyth

Received October 16, 1931. *Read and discussed February* 5, 1932

ABSTRACT. Methods previously available for the determination of the moisture-content of seeds are summarized and discussed. Two new methods are described, the first involving the use of a thermionic oscillator, the second a direct-current galvanometer and a battery. The first method is best suited for use with large-grained seed, whilst the second can be used for all types of seed.

§ 1. INTRODUCTION

THE work described in this paper was undertaken at the request of the Welsh Plant Breeding Station, Aberystwyth. Part of the work of this Station consists of large-scale production of pedigree grass and clover seeds, and since the keeping and germinating properties of seeds are largely dependent on their moisture-content, it is necessary to carry out, each season, a large number of moisture-content determinations. Hitherto these determinations have been carried out by the heat-drying method, which consists in grinding the seed and then heating it to about 98° C. until constant weight is obtained; the moisture-content can then be calculated from the initial and final weight of the seed taken. The disadvantages of this method are (i) that it requires a number of accurate weighings and (ii) that it is incapable of being carried out rapidly.

The aim of the experiments described below was to develop an instrument which would enable the moisture-content of seeds to be determined rapidly by a person who has not received any special training in accurate observation. It is thus necessary that the instrument, in addition to giving a reasonably accurate result rapidly, should be simple in principle, direct-reading, permanent in calibration and free from any complicated preliminary adjustments; in addition, it should preferably be portable.

§ 2. METHODS AVAILABLE FOR MOISTURE-CONTENT MEASUREMENT

The methods used nowadays for moisture-content measurement can be divided into two main classes, electrical and non-electrical. The latter class includes such methods as (i) the heat-drying method, described above; (ii) the oil-distillation method, sometimes called the Brown-Duval method (this consists in soaking the seed in a liquid which is immiscible with water and whose boiling point is higher than that of water; the mixture is then distilled and the moisture-content is determined from the relative proportions of oil and water in the distillate); (iii) the acetylene method. In this the moisture-content of the seeds is calculated from the amount of acetylene generated on the mixing of a known weight of seed with calcium carbide.

Two electrical properties appear to be suitable as a basis for moisture-content measurement—dielectric constant and resistivity; both these quantities should vary with moisture-content. Two electrical methods have been published—the Burton-Pitt method[1] and the Berliner-Rüter "D.K." method[2].

The Burton-Pitt method depends on the change in the d.c. component of the anode current of an oscillating thermionic valve, the change being brought about by inserting a glass vessel filled with seed in the oscillatory-circuit coil. The change in direct anode-current may be caused by (*a*) a change in the effective inductance and resistance of the coil due to eddy currents induced in the seed, or (*b*) a change in the self-capacity of the coil due to change in the dielectric constant of part of its surroundings. Calculation shows that the change in the effective resistance and inductance of a coil, due to the insertion of a core of resistivity equal to that of seed, is very small indeed. In fact, Belz[3], using the sensitive heterodyne-beat method, has shown that this eddy current effect is negligible even at radio frequencies for a highly conducting liquid such as concentrated sulphuric acid, provided that the coil is electrostatically screened from the core. Burton and Pitt apparently did not use an electrostatic screen and hence it is probable that the effect in their case is due to change in dielectric constant.

The Berliner-Rüter method depends directly on variation of dielectric constant with moisture-content. The dielectric constant is measured at radio-frequency by the following method. A valve oscillator is coupled through an intermediate aperiodic circuit to a low-decrement circuit of fixed capacity and fixed inductance. The intermediate circuit contains a sensitive current-indicator, by means of which resonance between the oscillator and the fixed-frequency circuit can be detected. By variation of its capacity the oscillator is initially tuned to the fixed-frequency circuit. A parallel plate condenser containing the seed is then placed in parallel with the oscillatory circuit, whose capacity is then varied until resonance is restored.

These two methods give rapid results, the time required for a moisture-content determination being a minute or so. The Burton-Pitt method suffers from two disadvantages: (i) great sensitivity is difficult to obtain without the use of a d.c. amplifier or an arrangement for balancing out the initial steady anode current;

(ii) the preliminary adjustments to repeat calibration conditions are somewhat complicated. It has the advantage of giving direct readings on a pointer instrument, and can thus be used by unskilled persons. The main disadvantage of the Berliner-Rüter method is that it requires an adjustment for resonance, and is thus not so simple to use as the Burton-Pitt method. The permanency of calibration of the Berliner-Rüter method is probably better than that of the Burton-Pitt, since the former is, to a certain extent, a null method. Another disadvantage of the Berliner-Rüter method is that the sharpness of the resonance-indication diminishes rapidly as the moisture-content increases, owing to the resistance of the seed-vessel becoming more comparable with its reactance. This disadvantage can be countered by increasing the frequency, but this, in turn, increases the disturbing effects of stray capacities. Both methods suffer from the drift effects usually associated with valve oscillators.

It should be noted that all methods described above, with the exception of the heat-drying method, are empirical and thus require calibration by means of samples whose moisture-content is determined by the latter method. Furthermore, a separate calibration is required for each type of seed to be tested. These remarks are equally true as regards the methods developed by the author, which will now be described.

§ 3. THE VALVE-OSCILLATOR METHOD

This method probably involves the dependence of both dielectric constant and resistivity on moisture-content. It had been developed before the work of Berliner and Rüter had been brought to the author's notice, and since it differs from the latter in its mode of action it will be described briefly.

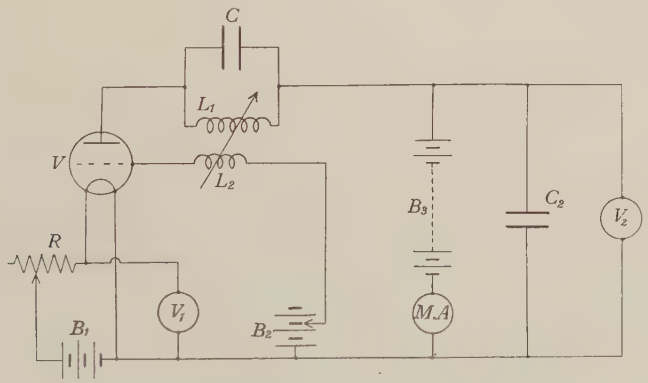

Fig. 1. Diagram of valve-oscillator circuit.

The apparatus consisted of a valve oscillator using magnetic reaction as shown in figure 1. The anode coil L_1 was a closely-wound, single-layer solenoid with 120 turns of double-silk-covered copper wire, s.w.g. 22, on an ebonite former of diameter 8·8 cm. The inductance of L_1 was approximately 800 μH. and its d.c. resistance 1·5 ohms. The grid coil, L_2, consisted of 100 turns of double-silk-covered copper wire, s.w.g. 40, wound on a presspahn former which just slipped over the

coil L_1. C_2 is a 2-μF. condenser used to by-pass radio-frequency currents from the anode battery, B_3, and the d.c. milliammeter MA. Across L_1 was connected a stand consisting of two insulated vertical aluminium strips mounted on an ebonite base; a parallel-plate condenser consisting of two square aluminium plates of side 10 cm. could be inserted between the vertical strips, which were provided with a spring arrangement to give good rubbing contact between the plates and the strips.

The moisture-content determination consisted in measuring the direct anode current indicated by MA, first with the empty condenser and then with the condenser filled with the seed under test. The change i_a in anode current thus obtained was found to be a function of the moisture-content of the seed used.

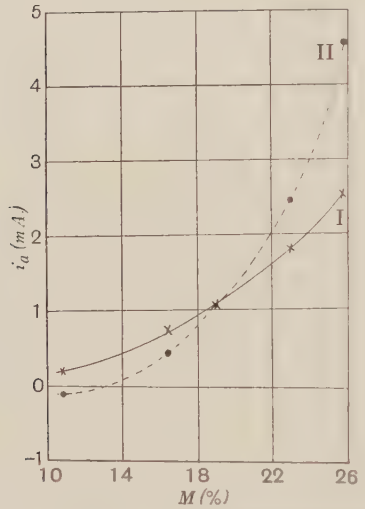

Fig. 2. Calibration curves of valve-oscillator apparatus for cocksfoot seed.

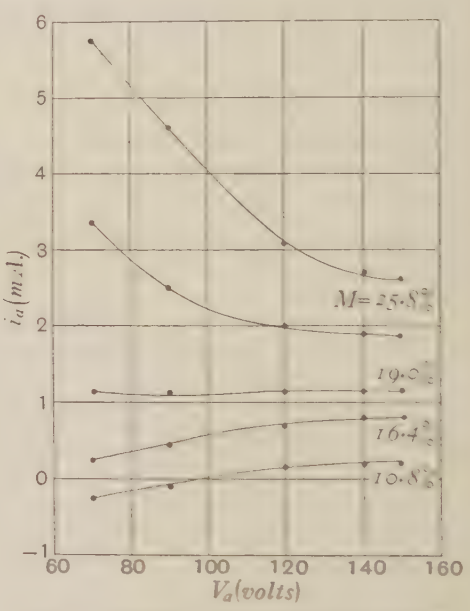

Fig. 3. Variation of anode current change with anode potential.

Figure 2 shows typical calibration curves for cocksfoot seed; moisture-contents M are taken as abscissae, and changes i_a in anode current as ordinates. The voltage V_f across the filament was 3·8 V.; the grid was connected directly to the negative end of the filament. In curve I, the anode voltage V_a was 150 V. and the initial value of the anode current 10·55 m.A.; in curve II, V_a was 90 V. and the initial value of the anode current 8·35 m.A. The valve used in these experiments was a Marconi-Osram L.S. 5 b. Experiment showed that the sensitivity of the apparatus is greatest when a valve of high amplification-factor is used. It was found, however, that the stability of the apparatus was far from good when a gettered valve, of the type used in broadcast-receiving sets, was employed; far better stability is obtained with a bombarded valve, especially when the valve is run at a filament voltage less than the makers' rating. Under these conditions, the permanency of calibration of the apparatus is likely to be good also.

The main disadvantage of this method is the number of variables involved; changes in anode and filament voltages especially affect the value of i_a corresponding to a given moisture-content. By suitable choice of these voltages it is possible to arrange matters so as to make the effect of such changes a minimum.

Figure 3 shows the variation of i_a with anode voltage V_a for different moisture-contents M; the filament voltage V_f was maintained constant at 3·8 V.

Figure 4 shows the variation of i_a with V_f for different values of M; V_a was maintained constant at 150 V.

From these diagrams, the slope of the i_a/V_a curves is seen to be a minimum when $V_a = 150$ V.; this, therefore, is the optimum value of V_a. In the case of the i_a/V_f curves, the value of V_f for minimum slope differs for different values of M; when $V = 3{\cdot}8$ V. the slope is a minimum for values of M lying between approximately 10 per cent. and 20 per cent., and since this is the most important range the optimum value of V_f is taken as 3·8 V. These diagrams show that the indications

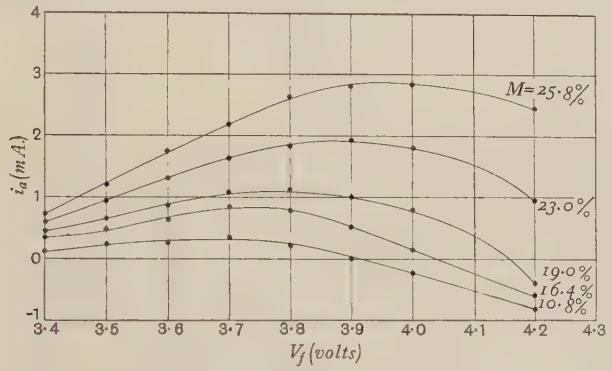

Fig. 4. Variation of anode current change with filament potential difference.

of the instrument can be made independent of the variations of V_a and V_f likely to occur in practice by suitable choice of the values of these quantities. In practice it is easy to dispense with the filament voltmeter V_1 and the anode voltmeter V_2, since it is possible to devise a simple switching system incorporating suitable series resistances which will enable the milliammeter MA to be used for these purposes. It is found, however, that the filament-voltmeter connexion is unnecessary, since the steady anode current I_a with no seed in the condenser is a sufficient index of the filament voltage, provided that the anode voltage has its calibration value. Accordingly, the simplest procedure is to adjust the anode voltage to its calibration value, and then, when conditions have become steady, to adjust the filament rheostat R_1 until I_a is at its calibration value.

I_a

It is interesting to calculate the possible error in the evaluation of moisture-contents by this procedure, assuming that the anode voltage can be set to within 1·5 V., as would be the case when a dry battery is used as the source of anode potential. When $V_f = 3{\cdot}8$ V. and $V_a = 150$ V., $I_a = 10{\cdot}55$ mA.; if V_a is reduced to 140 V., V_f has to be increased to $3{\cdot}82_7$ V. to obtain the same value of I_a. (This value

is found by plotting I_a against V_f, V_a being constant and equal to 140 V.) By drawing a family of curves similar to those in figure 4, but for a value 140 V. of V_a, the value of i_a can be found for different moisture-contents when $V_f = 3{\cdot}82_7$ V. Table 1 shows the values of i_a corresponding to various values of M with two different sets of values of V_a and V_f which give the same value of I_a. These were as follows: (*a*) $V_f = 3{\cdot}8$ V.; $V_a = 150$ V.; $I_a = 10{\cdot}55$ mA. (*b*) $V_f = 3{\cdot}82_7$ V.; $V_a = 140$ V.; $I_a = 10{\cdot}55$ mA.

If i_a be plotted against M, it is seen that the maximum difference in M due to the difference in i_a in the two cases is 0·6 per cent. Thus, for a difference of 1·5 V. in V_a, I_a being set in each case at its calibration value as described above, the maximum difference in M will be 0·09 per cent.

Table 1.

M (%)	i_a under conditions (*a*) (*mA.*)	i_a under conditions (*b*) (*mA.*)
10·8	0·2	0·15
16·4	0·8	0·75
23·0	1·15	1·10
25·8	2·60	2·80

As regards the accuracy of this apparatus, anode currents can be read to within 0·02 mA. when a meter with a $4\frac{1}{2}$-inch scale is used; a change of 0·02 mA. in i_a is equivalent to a change of 0·2 in M for values of M approximating to 10 per cent, and a change of 0·06 in M for values of M approximating to 25 per cent. Owing to unavoidable variations due to packing and similar causes, the real accuracy of the apparatus will be less than these figures; probably moisture-contents can be determined to within 0·6 per cent when the moisture-content is about 10 per cent, and to within 0·2 per cent when the moisture-content is about 25 per cent. It is interesting to note that, with the adjustment procedure described above, the limits of accuracy of the instrument are not exceeded if considerable variations in anode potential occur.

This method was found to work very well with coarse smooth-skinned seed, such as cocksfoot, and it can be used for the routine testing of this type of seed; such seed "packs" consistently without the use of pressure. When the method was tried with timothy seed, difficulties due to inconsistent packing were encountered; this is due to the fact that timothy seed is fine, is not smooth-skinned, and tends to adhere in one loose mass. Pressure is necessary to obtain consistent packing, and the parallel-plate condenser described above is inconvenient in this connexion.

The advantage of this method over the Burton-Pitt method is its greater sensitivity, while it is more suitable for unskilled use than the Berliner-Rüter method, since the indications are obtained on a pointer instrument.

§ 4. THE DIRECT-CURRENT RESISTANCE METHOD

This method, although designed primarily for fine seed such as timothy seed, gives satisfactory results with coarse seed such as cocksfoot seed or oats, as well as with finely-powdered substances such as flour. The method employed is to measure the ohmic resistance of the substance contained in a suitable vessel; with the vessel employed and the moisture-contents encountered in practice, this resistance is of the order of a few megohms. It is unnecessary to use alternating current for testing, since experiment shows that consistent results can be obtained with direct current. Two convenient methods can be used for testing: (i) measurement of the current due to a battery of 40–100 V. with a microammeter; (ii) a megger method.

As was pointed out above, the main difficulty in the design of a moisture-tester to give satisfactory results with seed similar to timothy seed is the difficulty of ensuring consistent packing. This can be overcome by use of the testing-vessel shown in figure 5 *a*. This consists of a brass tube *A*, closed at its lower end by an

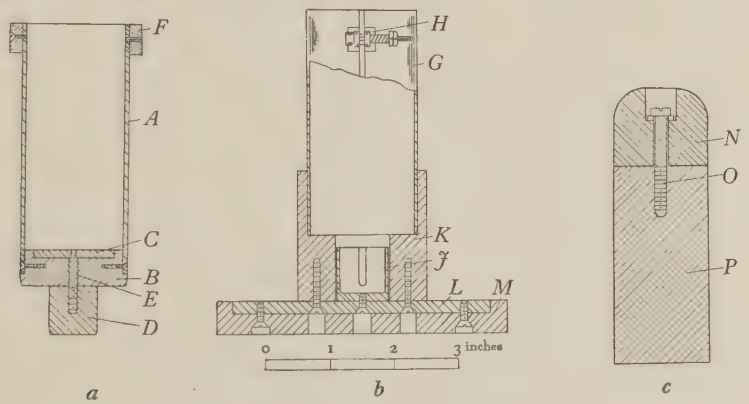

Fig. 5. *a*, Seed vessel; *b*, seed-vessel holder; *c*, plunger.

ebonite plug *B*, into which is sunk a brass disc *C*. This disc is fixed to the solid brass rod *D* by means of the screwed brass rod *E*. For convenience in handling, the upper end of the vessel is fitted with an ebonite ring *F*. The two electrodes used in the resistance-measurement are the cylinder *A* and the disc *C*. A convenient stand for the seed vessel is shown in figure 5 *b*. The cylinder *A* of figure 5 *a* fits into the brass cylinder *G*, which is split along its length and is fitted with the spring arrangement *H* to ensure good rubbing contact. The rod *D* of figure 5 *a* similarly fits into the brass cylinder *J*, which is split into four sections along part of its length. *G* is fixed into the ebonite base *K* which serves to insulate it from *J*. *J* is fixed by a screw to the brass plate *L*, which is embedded in the ebonite disc *M*. Connexion may thus be made between the external circuit and the electrodes through *G* and *L*. Figure 5 *c* shows the plunger used for applying pressure to the seed; it consists of a lead weight *N* fixed to the ebonite cylinder *P* by means of the screw *O*.

The advantages of using a seed vessel of the form shown is two-fold. In the

first place, consistent packing can be obtained by filling the vessel with the seed under test, pressing the plunger as hard as possible by hand and then releasing the pressure. In the second place, the resistance of the vessel when it contains seed packed as described above is independent of the quantity of seed present, provided that the level of the seed exceeds a certain limit determined by the dimensions of the vessel. This is due to the fact that the lines of flow of current between the disc and cylinder are closest in the lower part of the vessel, and thus it is the seed contained within this part that contributes most to the resistance between the two electrodes. To investigate this point further, dilute zinc sulphate solution was placed in the seed vessel, and the resistance between the two electrodes was measured by the ordinary a.c. bridge method for various heights of electrolyte. Figure 6 represents graphically the results obtained. The abscissae represent the height h of the liquid

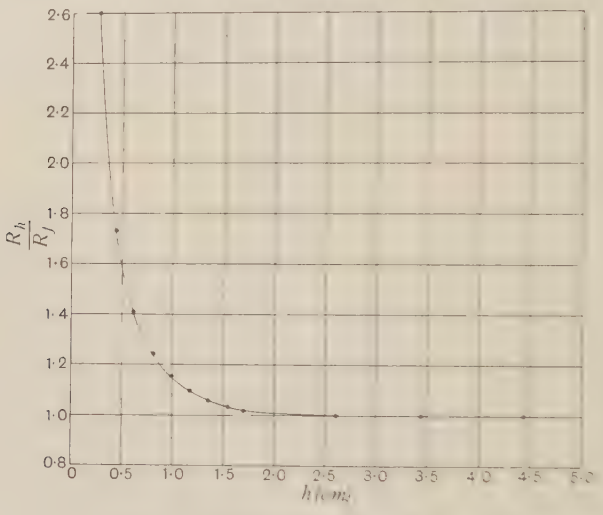

Fig. 6. Variation of resistance of seed with depth of medium.

in the vessel in cm.; the ordinates represent the ratio R_h/R_f where R_f is the resistance of the vessel when filled with the electrolyte, and R_h the resistance when filled to a height h. It is seen that R_h is independent of h provided that the latter is greater than 2·6 cm., whilst the value of R_h when h is 2 cm. is only 1 per cent greater than its limiting value. Experiment showed that when the vessel was initially filled with timothy seed and the seed then packed as described above, the height of the seed in the vessel was about 2·5 cm.; deliberate variation of the amount of seed initially introduced was then tried, and it was found that in no case likely to occur in practice would h be less than 2·3 cm. It is thus seen that variations in the quantity of seed introduced can be neglected—an important feature when the instrument has to be used by unskilled observers, and when the seeds under test tend to adhere together.

The two d.c. resistance methods mentioned above were investigated and found to be satisfactory. Since the battery and microammeter method is considerably cheaper than the megger method, the former was finally adopted. One fact should,

however, be mentioned; it was found that the resistance between the electrodes with packed seed depends on the applied voltage and on the previous history of the seed. Figure 7 shows the variation with applied voltage V, of the resistance R (in megohms) of timothy seed of approximately 14 per cent moisture-content; this sample had not been previously tested in the moisture-tester. The full curve was obtained on increasing V step by step to 370 V., and the broken curve on decreasing V step by step from this value. If the same sample of seed were again subjected to an applied voltage less than 370 V., its resistance would be appreciably different from either of the values shown on the curves. It is difficult to suggest an explanation for this phenomenon; it appears to be due to some kind of polarization within the seed. Any attempt at an explanation is complicated by the colloidal nature of

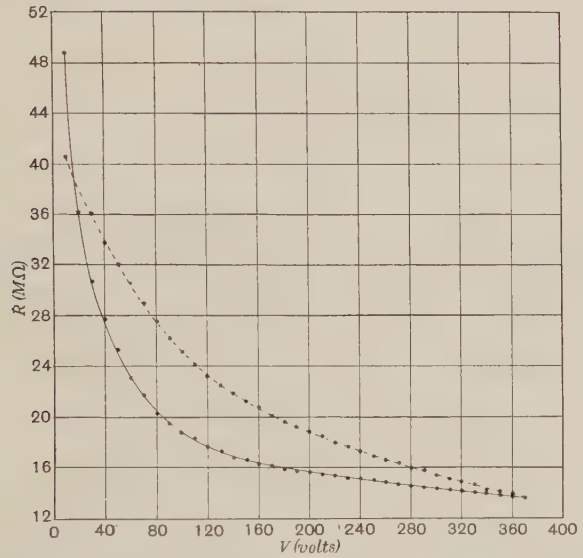

Fig. 7. Variation of seed resistance with applied potential.

the seed, since electro-osmosis and cataphoresis will be involved. This dependence of resistance on applied voltage does not in any way vitiate the method, provided that a constant voltage be used for calibration and testing; this can easily be arranged when using the battery and microammeter, by incorporating a switch to enable the microammeter to function as a voltmeter and thus to check the battery voltage. If a megger method be adopted, an instrument incorporating a constant-voltage generator should be used.

In its final form, the apparatus was connected up as shown in figure 8, in which A represents the seed vessel, and G a microammeter permanently shunted so as to give nearly full-scale deflection with the wettest seed likely to be encountered in practice. B is a dry battery whose voltage can be adjusted in steps of $1\frac{1}{2}$ V., whilst S is a three-pole three-position switch of the type used in wireless sets. R_1 is the usual series resistance for converting a microammeter into a voltmeter; R_2 is a shunt resistance brought into action when the microammeter is used as a voltmeter. The

purpose of R_2 is to reduce the sensitivity of the microammeter so as to obtain a reasonable value for R_1, which would otherwise be of the order of 2 to 3 megohms. When the switch S is in the right-hand position, G is in series with A, R_1 and B; the apparatus is then ready for seed-testing. The central position of the switch is an off position. When the switch is to the left, A is short-circuited while G is shunted by the resistance R_2 and is in series with the resistance R_1; it then functions as a voltmeter. In the instrument constructed the battery voltage used for testing was 45 V.; the resistance R_1 was 100,000 ohms, whilst G was an Onwood pointer galvanometer shunted so as to give full-scale deflection for about 500 μA. It will be noticed that the resistance R_1 is permanently in circuit; for seeds of low moisture-content (10–15 per cent) its presence is immaterial; with seeds of medium moisture-content (15–30 per cent) it tends to make the calibration curve less steep; with very

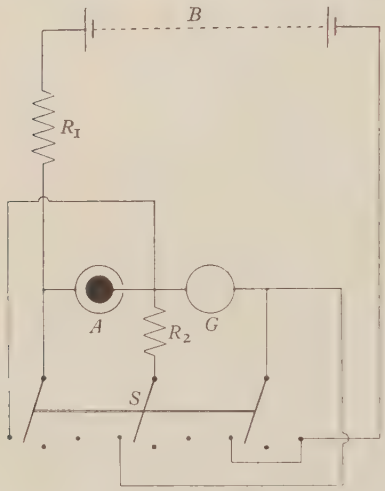

Fig. 8. Diagram of connexions of resistance method apparatus.

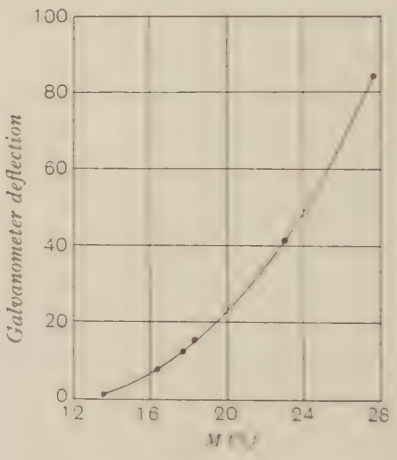

Fig. 9. Typical calibration curve of resistance method apparatus for timothy seed.

wet seeds (30 per cent and over) it makes the slope of the calibration curve small, since the resistance of R_1 is large in comparison with that of the seed vessel under these conditions. This last effect is not detrimental, since seeds containing more than 30 per cent of moisture are seldom encountered.

Figure 9 shows the calibration curve of the instrument for timothy seed; galvanometer deflections are taken as ordinates and moisture-contents M as abscissae.

To using the instrument, the following procedure is followed. (i) The switch S is turned to the left-hand position and the battery voltage adjusted to its calibration value. (ii) The switch S is turned to the central position and the seed vessel filled and packed as described above. The seed vessel is then inserted in its stand, and, when the microammeter pointer has become steady, the switch is rotated to the right-hand position. (iii) The moisture-content of the seed is found by reference to the calibration table giving the moisture-contents corresponding to each division on the galvanometer scale.

This apparatus has now been in use for some months and has been found to work satisfactorily; the accuracy of the instrument is such that it will give readings on any part of its scale which differ by less than 0·1 in moisture-content.

Its chief advantages are (i) the simplicity of principle and construction; (ii) the ease and rapidity of the moisture-estimation, readings being obtained with a pointer; (iii) the preliminary adjustment to reproduce calibration conditions is simple and, moreover, is not frequently required; (iv) the permanency of calibration; (v) the sensitivity is adequate, and can be varied to suit different conditions by varying the testing voltage or, alternatively, by varying the sensitivity of the microammeter.

It is proposed to extend the use of the instrument to the measurement of the moisture-content of grasses and root crops. In the former case the grass will be cut up by passing it through a miniature chaff-cutter; in the latter case it is proposed to use two insulated spikes inserted in the root as electrodes.

§ 5. ACKNOWLEDGMENTS

The work was carried out at the Department of Physics, University College of Wales, Aberystwyth, and the writer wishes to acknowledge his indebtedness to Prof. Gwilym Owen for his constant help and encouragement, to Prof. R. G. Stapledon and Mr Gwilym Evans of the Welsh Plant Breeding Station for the various seeds used, and to Prof. T. W. Fagan of the Agricultural Chemistry Department for the determination of the moisture-contents of the seeds used for calibration.

The apparatus is being manufactured by Messrs A. Gallenkamp and Co., Ltd., Technico House, Sun Street, London, E.C. 2.

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DISCUSSION

Dr Ezer Griffiths. The paper will be of interest to those concerned with the determination of the moisture-content of materials such as wool, cotton, etc. The author might with advantage state what concentration of a salt solution gives a resistance comparable with that of the seeds tested. One would also like to know more of the mechanism of the electrical conduction and the mode of distribution of the flow lines in an individual seed.

A practical detail which needs consideration is the state of the surface of the narrow annular ring of ebonite separating the two electrodes. If moisture collects on this surface then troubles due to surface leakage would arise.

Mr G. R. Stanbury. Mr Davies's paper is very interesting to us on account of some similar experiments we have been carrying out on the rapid estimation of the moisture-content of textile fibres. Professor Burton left his apparatus with the

Wool Industries Research Association for this purpose when he was over here eighteen months ago, and it was exhibited at the Physical Society's Exhibition in 1931. We agree with Mr Davies regarding certain of the disadvantages of the apparatus, but we fail to see in what way the valve-oscillator method described in § 3 is any improvement, as the circuit used is identical with that of the Burton-Pitt instrument. The only apparent difference is that the moisture-containing material is introduced into the condenser instead of between the coils as described by Burton and Pitt. This alternative had, however, already been provided for in the apparatus loaned to us, but it was not found to give any more reliable results. We disagree with the statement that with the Burton-Pitt instrument it is difficult to obtain great sensitivity, since we have obtained plate-current changes of equal order to those given in figure 2 for similar conditions. The sensitivity depends purely on the values of the various electrical quantities involved. The main disadvantage from our point of view is the difficulty of repeating calibration conditions, and the fact that the calibration curves vary with almost every conceivable type or quality of wool and the method of packing. The direct-current-resistance method offers greater promise and the method adopted for overcoming the necessity for accurate measurement of samples is very ingenious. In experiments carried out on single wool fibres we have noticed the same hysteresis effect as shown in figure 7.

Has the author's attention been called to another direct-current-resistance method for grain which is being marketed by the C. J. Tagliabue Mfg. Co., Brooklyn? In this method a certain quantity of the grain is allowed to pass between two rotating rollers which act as electrodes, the average deflection of the galvanometer pointer being a measure of the moisture-content of the grain.

Mr D. K. McCleery. I should like to ask what interval elapsed between the application of the battery and the reading of the current, and also whether any variation of the current with time was noticed. It is the usual commercial practice in testing dielectrics to observe the resistance after the potential has been on for one minute, but everyone knows that this is purely arbitrary though it serves as a rough basis of comparison. To wait until the absorption current has died away, leaving only the leakage current, would require infinite patience in most cases; hence the necessity for a standard time-interval. In the present case the method is described as "rapid," so it is inferred that this interval was not great.

The curve shown in figure 7 is similar to the results obtained by Evershed* in his tests of cotton and paper under various conditions of humidity. The application of the superposition principle of Hopkinson† to such a case is complicated owing to this characteristic. We may suppose that the current through the seed under a potential V applied at $t = 0$ is expressed by

$$i = V^n \phi(t) \qquad \text{.....(1),}$$

$n, \phi(t)$ where n and $\phi(t)$ are experimentally determined.

r If the potential is applied in r small steps each equal to V/r and acting at times

* S. Evershed, *J. Inst. E. E.* **52**, 51 (1914). † J. Hopkinson, *Original Papers*, Nos. 18, 19.

0, t_1, t_2 ... t_{r-1}, instead of all at once then, by the superposition principle, the current i is given by t_r

$$i = (V/r)^n \{\phi(t) + \phi(t - t_1) + \phi(t - t_2) + \ldots + \phi(t - t_{r-1})\} \quad \ldots\ldots(2).$$

Now if the function $\phi(t)$ decreases with time, as in the case of a normal dielectric, we should expect the current in (2) to be greater than in (1); or, in other words, the resistance after time t to be less when the potential is stepped up than when it is applied completely at $t = 0$.

When the potential is reduced to the level V', at time t_r for example, the apparent resistance will be higher than if it had been raised to V' at $t = 0$, and if it is reduced step by step then by the above argument the resistance will *a fortiori* be higher. This may be the explanation of the fact that the broken curve in figure 7 lies above the full curve. In conclusion I should like to urge that a constant time-interval is no less important than a constant voltage.

Mr J. H. Coste. The author, in his interesting paper, is obviously speaking from the point of view of a physicist in classifying methods of determining moisture as electrical and non-electrical. As a chemist I should feel inclined to describe them as direct and indirect. Some time ago I devoted much attention to this apparently very simple determination in relation mainly to fuel. The international committee of which I was vice-president found that it was advantageous to dry at 105–110° C. rather than at about 98° C. as mentioned by Mr Davies (the temperature is often much lower in parts of a water oven), and we were inclined to prefer for precise work drying in an inert atmosphere and absorbing the water in a weighed tube containing a desiccant, or the very slow process of drying in a vacuum. The xylene method (Brown and Duval), in which the water distilled off with the solvent is measured, is a good one, as also is the acetylene or carbide method.

The author has described two methods of determining physical properties of seeds, the variation of which properties he associates with variations of water-content. The object of his work is fairly described in § 2 of the paper and clearly the more *ad hoc* methods which they are intended to replace do not lend themselves to mass production by unskilled labour.

The precision required of moisture-determinations in a seed-testing establishment is probably not high, but in mentioning the sensitiveness of his apparatus the author is not describing its accuracy, and I think he would add to the value of the paper if he gave a table of comparative determinations of moisture in different kinds of seeds by a recognized *ad hoc* method and by, say, his second method which seems to be the more generally useful.

In figure 7 he shows how the resistance of an aggregate of seed varies with applied potential. One is inclined to wonder whether the (admittedly very small) heating effect of the applied current on the seed-aggregate tested causes either evaporation of water which is partly reabsorbed as the voltage is decreased, or whether the increase which it must produce in the degree of ionisation of the salts in the seed causes the observed reduction in the resistance. The electrolysis caused by a direct current also introduces some complication.

In attempting to apply the second method to roots it will be necessary to remember that what is really being measured is the resistance of a dilute solution of salts, as these contribute mainly to the conductance of such vegetable substances. The specific conducting of pure water is very low—Kohlrausch and Heydweiller found it to be $0{\cdot}04 \times 10^{-6}$ ohms^{-1}-cm.$^{-1}$, and ordinary tap water owes its relatively high conductivity to the dissolved salts.

I cannot consider the theoretical basis of either process as very well established, but I am prepared to believe that both may be very useful for the purpose for which Mr Davies designed them, provided periodical check determinations are made by a recognized method.

Author's reply. In reply to Dr Ezer Griffiths: The resistance of the vessel when filled with seed is of the order of megohms, and it is of the order of 50 ohms when filled with distilled water to which a few cubic centimetres of normal zinc sulphate solution has been added.

No case of deposition of moisture on the ebonite insulation between disc and cylinder in the seed-vessel has yet been brought to my notice, although several hundreds of tests have been made with the instrument. Deposition of moisture in this way is easily detected by making an observation with the empty seed vessel, in which case a deflection indicates faulty insulation. In the instructions for use accompanying the instrument it is recommended that this insulation test be frequently applied, especially when testing very wet samples. If the insulation be found faulty in this respect it can easily be rectified by rubbing with a silk rag moistened with methylated spirits, and then drying.

In reply to Mr Stanbury: I was unaware of the fact that the Burton-Pitt apparatus incorporated an arrangement for introducing the moisture-containing material into the condenser; there is no mention of this in either of the two papers mentioned above, neither was it apparent in the instrument shown at the Physical Society Exhibition in 1931. I agree that a sensitivity comparable with that shown for my first apparatus is obtainable with the Burton-Pitt apparatus, but under these conditions the latter is very unstable. The data shown in figure 2 were obtained with a perfectly stable apparatus, the optimum working conditions being determined by the experiments described on pages 234, 235; under these conditions it is possible to repeat calibration conditions exactly. Greater sensitivity than that shown in figure 2 is obtainable with my apparatus, but always at the cost of stability.

It is interesting to note that a hysteresis effect is also obtained with single wool fibres and this property may well be characteristic of organic material.

I was unaware of any details concerning the Tagliabue Moisture Meter when my paper was written; a complete detailed account does not appear to be available. It is stated, however, that the grain-meter is "similar in principle to the lumber moisture-meter," and the latter is definitely a valve method.

In reply to Mr McCleery: The procedure adopted in the direct-current-resistance method was to insert the packed seed vessel in the apparatus and then switch on the testing voltage; the galvanometer was read as soon as the pointer had come

to rest. The galvanometer used was of the Onwood type and this necessarily takes some time to come to rest; with the range of moisture-contents covered in my experiments and with the testing voltage used, the galvanometer reading then remained constant, so that the need for a constant time-interval for testing was eliminated. With the higher voltages used in the experiments of figure 7, the time effect was noticeable, and this is why a comparatively low voltage (40–60 V.) is used for testing. This time effect was also encountered in some experiments where abnormally wet seeds were used.

Mr McCleery's application of Hopkinson's principle of superposition is interesting and deserves more detailed investigation, particularly as to the values of n and ϕ; it certainly does give a possible explanation of the hysteresis effect of figure 7 in terms of phenomena observed with a steady testing voltage.

In reply to Mr J. H. Coste: As was pointed out in this communication, the absolute determination of moisture-content is by no means a simple experiment, and considerable discrepancies are shown by methods such as the Brown-Duval and the oven method, which are our closest approximation to absolute methods. The difficulty is enhanced in the case of seeds, since chemical decomposition occurs if their temperature is raised above 98° C. or so. The acetylene method is good in principle, but suffers from the defect that it can only be used for purely pulverized substances such as flour; it is quite inapplicable to seeds, mainly because of the hard husk which surrounds the seed nucleus.

As to the accuracy and permanency of calibration of my direct-current-resistance method, the apparatus contains only one variable factor, the battery voltage; and variations in this are immediately detectable. Tests show that the permanency of calibration is better than 0·1 per cent in moisture-content. Mr Coste's remarks as to the explanation of the hysteresis effect of figure 7 merit further investigation, although the heating effect must necessarily be very small with currents of the order of 100 μA. The methods described have admittedly no theoretical basis apart from the fact that the electrical conductivity of a seed aggregate is definitely a function of the moisture-content of this aggregate. It may be added that the methods described—especially the second method—fulfil their function admirably.

THE COLLISIONAL FRICTION EXPERIENCED BY VIBRATING ELECTRONS IN IONIZED AIR

By E. V. APPLETON, F.R.S. and F. W. CHAPMAN, M.Sc.

Received December 30, 1931. *Read and discussed February* 5, 1932

ABSTRACT. The variation of the radio-frequency conductivity of ionized air with pressure has been studied experimentally at frequencies of the order of $10^8 \sim$. From the measurements of the critical pressure at which such conductivity is a maximum the magnitude of the collisional frictional forces experienced by vibrating electrons has been estimated.

§ 1. INTRODUCTORY

Previous laboratory investigations of the radio-frequency properties of ionized air have been largely confined to the study of the dielectric constant of such a medium and, in particular, to the confirmation of the theory that the dielectric constant can, under certain conditions, be less than unity. In such experiments radio-frequencies up to $10^8 \sim$ have been used.

The experimental investigations here described were carried out with a higher frequency range, up to $10^9 \sim$, and, although evidence of a dielectric constant less than unity has been observed incidentally, the observations are concerned chiefly with the radio-frequency resistance of the medium and with the variation of such resistance with pressure. Using ultra-short waves of wave-length 40 to 100 cm., produced by the method of Barkhausen and Kurz*, the existence of a maximum conductivity at a certain critical pressure for any given frequency has been demonstrated, and from the measurements of these critical pressures the magnitudes of the frictional forces experienced by the vibrating electrons have been deduced.

§ 2. THE RADIO-FREQUENCY CONDUCTIVITY OF AN IONIZED MEDIUM

The theory of the propagation of electromagnetic waves through an ionized medium was given by H. A. Lorentz† as early as 1909. From the results of Lorentz we can deduce, with only a slight modification, the expression for the radio-frequency conductivity of the medium which we use here.

m, e

Consider an electron, of mass m and charge e, vibrating in a gaseous medium

E, E_0, pt

under the influence of an alternating electric force $E = E_0 \sin pt$. Lorentz writes the equation of motion of such an electron as

$$m\frac{d^2x}{dt^2} + g\frac{dx}{dt} + fx = e\left(E + \tfrac{1}{3}P\right) \qquad \text{.....(1).}$$

* *Phys. Z.* **21**, 1 (1920).

† *Theory of Electrons*, p. 132 (Leipsig, 1909).

Here x represents the displacement and t the time; g is the frictional force suffered by the electron per unit velocity and f the restoring force per unit displacement. P is the polarization of the medium and is equal to Nex, where N is the number of electrons per cm^3. x, t, g f P, N

The symbols retaining the same significance, it is easy to show, from a comparison of the equations of Lorentz and the equations relating to the propagation of electromagnetic waves through a conducting dielectric, that we can regard the ionized medium as possessing a dielectric constant K and a conductivity σ given respectively by K, σ

$$K = 1 + \alpha/(\alpha^2 + \beta^2) \quad \text{.....(2),}$$

and

$$\sigma = p\beta/(\alpha^2 + \beta^2) \quad \text{.....(3),}$$

where

$$\alpha = f/Ne^2 - mp^2/Ne^2 - \tfrac{1}{3} \quad \text{.....(4),} \qquad \alpha$$

and

$$\beta = pg/Ne^2 \quad \text{.....(5).} \qquad \beta$$

It is the expression for the high-frequency conductivity σ with which we are here concerned. We note from (3), (4) and (5) that this may be written

$$\sigma = \frac{Ne^2 g}{\{(f/p - mp - Ne^2/3p)^2 + g^2\}} \quad \text{.....(6).}$$

Now Gutton*, from a very extensive series of researches, has come to the conclusion that electrons in an ionized gas are subjected to quasi-elastic forces giving rise to the existence of a resonance frequency which depends on the ionic concentration. Some experiments† carried out in this laboratory, while confirming the experimental results of Gutton, have, however, led to the conclusion that his deductions from his results are erroneous. All the quasi-resonance effects are to be explained, both qualitatively and quantitatively, as due to the fact that the dielectric constant of the ionized gas under the experimental conditions assumes negative values. We therefore shall assume the restoring force coefficient, f, to be zero, so that (6) becomes

$$\sigma = \frac{Ne^2 g}{(mp + Ne^2/3p)^2 + g^2} \quad \text{.....(7).}$$

The assumption that the restoring force acting on the vibrating electron is equal to zero raises a question relative to the magnitude of the frictional coefficient g. Lorentz, to whom the recognition of the effects of collisional friction is due, has shown that, for the case of bound electrons, we have

$$g = 2m/\tau \quad \text{.....(8),}$$

where τ is the average time between two collisions of an electron with the gas molecules. We believe, however, that the reasoning used by Lorentz‡ for bound electrons does not apply without alteration to the case of free-electrons. The following treatment is a revision of Lorentz's calculation assuming the charges to be free. τ

Consider an electron vibrating under the influence of a periodic electric force and subjected to gaseous collisions. We suppose that there is no real friction but

* See, for example, *Ann. de Physique*, **13**, 62 (1930).

† An account of these experiments will shortly be published by Dr J. Goodier and one of the authors.

‡ See H. A. Lorentz, *Theory of Electrons*, p. 309.

that the vibrations of the electrons are over and over again disturbed by impacts at irregular intervals. The equation of motion of the electron is

j $$m\frac{d^2x}{dt^2} = eE\epsilon^{jpt} \qquad \text{.....(9),}$$

v whence $$\frac{dx}{dt} = v = -j\frac{Ee}{mp}\epsilon^{jpt} + C \qquad \text{.....(10).}$$

If we consider (10) as applying to a large number of electrons for all of which the t_1 last collisional interruption of their motion took place at some time t_1, the mean value of their velocity at that instant will be zero, so that from (10) we have

$\overline{C}$ $$\overline{C} = j\frac{Ee}{mp}\epsilon^{jpt_1} \qquad \text{.....(11).}$$

To each electron of this group we can therefore assign a velocity given by

ϑ $$v = -j\frac{Ee}{mp}(\epsilon^{jpt} - \epsilon^{jpt_1}) = -j\frac{Ee}{mp}(1 - \epsilon^{-jp\vartheta})\epsilon^{jpt} \qquad \text{.....(12),}$$

where $$\vartheta = t - t_1 \qquad \text{.....(13).}$$

Following Lorentz, we may now say that since the collisions succeed each other irregularly we may reckon that the number of particles for which the interval lies N between ϑ and $\vartheta + d\vartheta$ is $(N/\tau)\epsilon^{-\vartheta/\tau}d\vartheta$, where N is the total number of particles τ considered and τ is the average time between two collisions.

Multiplying (12) by $(N/\tau)\epsilon^{-\vartheta/\tau}d\vartheta$, integrating from $\vartheta = 0$ to $\vartheta = \infty$, and dividing $\overline{v}$ by N we find that the mean velocity $\overline{v}$ of all the electrons is given by

$$\overline{v} = \frac{Ee}{m(jp + 1/\tau)}\epsilon^{jpt} \qquad \text{.....(14).}$$

Now if we assume a frictional coefficient for a vibrating electron we obtain the following equation for the velocity,

$$\overline{v} = \frac{Ee}{jpm + g}\epsilon^{jpt} \qquad \text{.....(15),}$$

so that for free electrons we obtain from a comparison of (14) and (15)

$$g = m/\tau \qquad \text{.....(16).}$$

We see, therefore, that since τ is inversely proportional to the gas pressure, g varies directly with the pressure.

Returning now to consideration of (7), we note that, if N is kept constant and g varied by an alteration of pressure, the conductivity is a maximum when

$$g = mp + Ne^2/3p \qquad \text{.....(17).}$$

Under the conditions of our experiments, however, the ionization was so small that the magnitude of the polarization term $Ne^2/3p$ was small compared with mp*, so that we write, simply,

$$g = mp \qquad \text{.....(18)}$$

as the condition for maximum conductivity.

* This statement is not strictly true for the higher values of tube current used, but the fact that, even under those conditions, the value of g was not found to vary with N, leads us to believe that polarization effects were still negligible.

We see therefore that if the value of N is kept constant and g varied, by variation of the gas pressure, there will be a maximum conductivity for the ionized medium at a certain critical pressure. At that pressure the value of g is given by mp. Our object, in the experiments described below, was to demonstrate the existence of this maximum conductivity and thereby estimate the value of g with the aid of (18). The ionized medium consisted of a low-pressure discharge, the high-frequency conductivity of which was studied by a method similar to that used by Van der Pol* in his study of the variation of conductivity along a glow discharge.

These experiments were supplemented by an exploring-electrode analysis of the discharge in question. This analysis was necessary for two reasons. In the first place, before we can associate any meaning with the observed variation of conductivity with pressure it is necessary to be certain of the constancy, or at least the law of variation, of N, the number of electrons per cm.^{3} with pressure over the pressure range used. Secondly, in order to be able to compare the experimentally-determined values of g with the theoretical value m/τ it is necessary to know the thermal velocity v of the electrons, from which, knowing the mean free path, the value of τ can be deduced. The use of a probe-electrode for the determination of electron concentration and electron velocity has been described by Langmuir and Mott-Smith†.

§ 3. EXPERIMENTAL ARRANGEMENTS

The discharge tube used (see figure 1) was 30 cm. long and 3 cm. in diameter, and fitted with nickel electrodes 2 cm. in diameter and 10 cm. apart. The electrodes were held in position on to a glass rod by means of small nickel clips welded on to them. A cold cathode discharge was maintained between them by means of a motor-generator, the discharge current being maintained constant by the inclusion of a saturated diode in series with the discharge. The discharge tube was set up vertically between two condenser plates KK which constituted the terminal capacity of a pair of Lecher wires, figure 2. An exploring electrode was also fused into the side of the discharge tube. This consisted of a short length of phosphor-bronze wire 0·0076 cm. in diameter which was welded on to a short nickel rod. The whole was sheathed in a glass tube which was drawn down to a small bore at one end, through which 0·3 cm. of the phosphor-bronze wire was allowed to protrude. Care was taken that the wire did not touch the glass at the point where it emerged from the sheath. The whole electrode system could be moved in relation to the condenser plates or to the exploring electrodes.

The condenser plates were of thin copper foil 4 cm. long and 3 cm. wide and were situated symmetrically with regard to the discharge tube, 3·5 cm. apart, and the electrode system was adjusted so that the Faraday dark space was between the plates. The Lecher system consisted of two copper wires of 16 s.w.g., 1 m. long, and 5 cm. apart. Instead of the usual wire bridge for resonance-adjustments a copper reflecting plate (P in figure 2), 30 cm. square, was used. This was fitted with sleeves so that it could be made to slide along the Lecher wires.

* *Phil. Mag.* **38**, 352 (1919). † *Gen. Elec. Rev.* **27**, 449 (1924).

Forced vibrations were produced in the Lecher-wire system by means of local ultra-short-wave triode generators. A wave-length range from 40 to 90 cm. was used.

The amplitude of the forced vibrations maintained in the Lecher-wire system was measured in arbitrary units by means of a galena crystal detector D, figure 2, and a dead-beat moving-coil galvanometer. The detector circuit was coupled to the

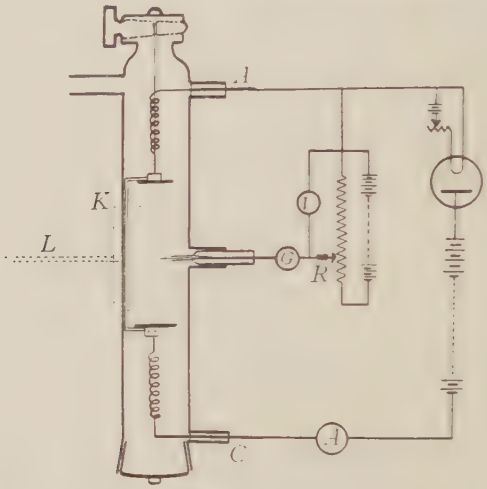

Fig. 1.

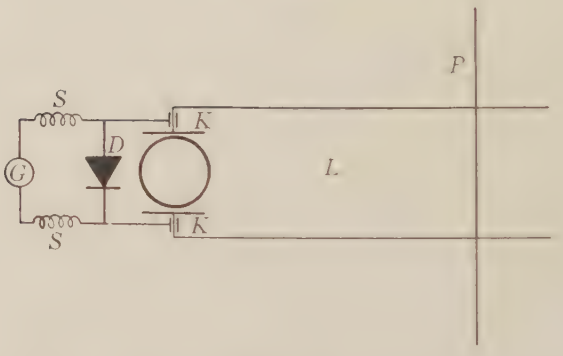

Fig. 2.

Lecher-wire system by means of two small condensers consisting of short brass tubes insulated from the Lecher wires by means of glass tubing.

The presence of a conducting dielectric, such as ionized air, between the condenser plates reduced the amplitude of the forced vibrations in the Lecher-wire system by an amount which was dependent on the conductivity. We have not attempted to relate conductivity to galvanometer-deflection but have merely assumed, as seems reasonable, that an increase of conductivity brought about a reduction of galvanometer-deflection.

§ 4. EXPERIMENTAL PROCEDURE

To study the relation between conductivity and pressure, the resonance deflection was first obtained for no ionization in the discharge tube. The discharge was then started for the minimum pressure in the range to be worked, and the system was then tuned again and the deflection noted. The pressure was allowed to increase in steps, and corresponding readings of pressure and resonance galvanometer-deflections were noted. Such observations were repeated for other wave-lengths and it was noted that the pressure for minimum deflection and therefore for maximum conductivity varied with the wave-length.

The values of electron-concentration N were determined by the now well-known methods of measuring the current to the probe as a function of the potential between the probe and the anode of the discharge tube. The measurements of N yielded the very convenient result that, even though the pressure of the discharge was varied, the maintenance of constant tube-current by the use of the diode ensured that N remained constant through the range of pressures used.

§ 5. EXPERIMENTAL RESULTS

In figure 3 is shown a typical series of results illustrating the relation between resonance amplitude in the Lecher-wire system and gas-pressure for two values of tube current. Since the galvanometer deflection decreases with increase of con-

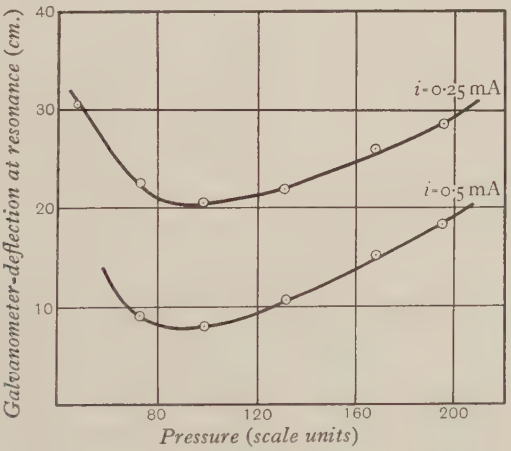

Fig. 3. Results relating to a wave-length of 80 cm.

ductivity of the ionized medium, the curves clearly demonstrate the existence of a maximum conductivity at a certain pressure, as predicted by theory.

In the table are collected the results for a range of wave-lengths. In the fifth column are given the values of g calculated from (18). The constancy of the last column indicates that g is proportional to the pressure for the range considered.

Table.

Wave-length λ (*cm.*)	p ($\sim \times 10^9$)	Pressure for maximum σ		g ($10^{-18} \times$ *dynes per unit velocity*)	A calculated as g/P (*e.m.u.* $\times 10^{-20}$)
		(*mm. of Hg*)	(*Microbars, P*)		
88	2·14	0·08	105	$1·9 \times 10^{-18}$	1·83
60	3·14	0·11	153	$2·8 \times 10^{-18}$	1·83
54	3·49	0·12	167	$3·1 \times 10^{-18}$	1·89
48	3·93	0·15	193	$3·5 \times 10^{-18}$	1·81

§ 6. DISCUSSION OF RESULTS

The results described above confirm the theory in so far as a maximum conductivity has been found at a certain pressure for a given frequency of the electromotive force. This result has possibly some significance in connexion with the absorption of wireless waves during their process of reflection by upper-atmospheric ionization; for, since the attenuation factor of wireless waves is proportional to σ, we see that for waves of a given frequency there will always be some particular height in the atmosphere at which a given ionization-content will produce maximum absorption.

The values of the frictional coefficient g which have been deduced from the observations show a proportionality with the gas-pressure. This is to be expected from the relation $g = m/\tau$, since τ varies inversely as the pressure.

An exact comparison of the experimental value of g with the theoretical value m/τ is hardly possible in view of our lack of accurate information concerning τ. But a rough comparison may be made as follows. Let us consider the case in which the wave-length used was 88 cm. and the critical pressure found to be 0·08 mm. For this pressure the mean free path of a nitrogen molecule is known to be 0·080 cm., so that the mean free path of an electron, which is $4\sqrt{2}$ times this value, is 0·45 cm. Now the probe analysis indicates that the electron-velocity corresponds to a fall of potential of about 6 V., a value which agrees with that obtained by other investigators for this type of discharge. This means that the electron-velocity was about $1·5 \times 10^8$ cm. sec., in which case the values of τ and $m\tau$ were 3×10^{-9} and 3×10^{-19} respectively. Now the experimental value of g for the pressure in question was $1·9 \times 10^{-18}$, a value 6·3 times as large as the calculated value of $m\tau$. We do not think that this discrepancy necessarily proves that the theoretical relation $g = m\tau$ is not valid, as our experimental conditions were not such as to favour a strict comparison of g and m/τ. The electron velocity was doubtless not constant across the cross-section of the tube. Also the positive ions in the sheaths next to the glass walls may have played a part in determining the variations of conductivity, in which case the mean free path would be smaller and the value of $m\tau$ correspondingly larger than in the case of the electrons. It is, however, possible to obtain another estimate of $m\tau$ in the following way. According to Langmuir and Compton the direct current mobility μ of electrons in a discharge is given by μ

$$\mu = 0·85 e\lambda/mv \qquad \text{.....(19).}$$

Now the drift current i per unit area is given by

$$i = Ne\mu\bar{E} \qquad \text{.....(20)},$$

where $\bar{E}$ is the electric force applied. Therefore from (19) and (20) we have

$$mv/\lambda = m/\tau = 0{\cdot}85Ne^2\bar{E}/i \qquad \text{.....(21)}.$$

For the body of the discharge we are considering, the value of $\bar{E}$ at a pressure of 0·08 mm. was found, from probe measurements of the space potential, to be about 1 V./cm. The current-density was known to be $1{\cdot}6 \times 10^{-4}$ A./cm.^{2} Also N for these conditions of current and pressure had been found to be $1{\cdot}5 \times 10^9$, so that on substitution in (21) we find that m/τ is 2×10^{-18}. This is very nearly the value of g obtained experimentally at the pressure in question.

Summarizing therefore we see that in the example chosen the experimental value of g was $1{\cdot}9 \times 10^{-18}$, while m/τ was estimated as $0{\cdot}3 \times 10^{-18}$ and 2×10^{-18} by two different methods. The agreement is, we think, as good as could be expected in view of the heterogeneous nature of the discharge and the fact that probe measurements could be made only at one point in a cross-section.

Before concluding this discussion one or two points of interest in connexion with the dielectric constant of an ionized medium may be mentioned. Various observers have found it difficult to demonstrate the existence of a dielectric constant less than unity. Van der Pol*, who was the first to examine this effect, used wave-lengths of 3 m. and only for very small electron concentrations found the dielectric constant diminished. For greater concentrations the apparent dielectric constant was greater than unity. Frl. Szekely†, working with wave-lengths between 242 and 58 m. found a dielectric constant greater than unity at all concentrations. In this connexion it should be noticed that the theoretical expression for the dielectric constant of an ionized medium does not permit values greater than unity, whatever the ionic concentration may be. As has been shown by Appleton and Childs‡, the increased dielectric constant, when measurements are made with internal electrodes, is due to the influence of the ionic sheaths which form round the electrodes.

When very short waves and external electrodes are used, as in the present experiments, the difficulty mentioned above disappears and it is very easy to demonstrate the existence of a dielectric constant less than unity. In figure 4 is shown the relation between Lecher-wire tuning and tube current for a wave-length of 80 cm. It will be seen that, even for the highest tube current we could use, the Lecher-wire length had to be increased to restore resonance conditions indicating that the capacity of the terminal condenser was reduced by the presence of the ionized medium. The interesting variation in this curve at A, which suggests some species of resonance effect, was repeatedly found, and is not believed to be spurious. It is possibly connected with the free period of the plasmoidal oscillations discussed by Tonks and Langmuir, since the relation between the wave-length and the electron concentration N at which the effect occurs is such as may be predicted from their theory. Since the wave-length λ was 80 cm. and since a tube current

* *Thesis, University of Utrecht* (1920).

† *Ann. der Phys.* **5**, 3, 112 (1929).

‡ *Phil. Mag.* **10**, 969 (1930).

of 450μA. was known to correspond to an electron concentration of $1{\cdot}62 \times 10^9$, we have $N\lambda^2 = 1{\cdot}04 \times 10^{13}$, while for resonance with plasmoidal oscillations for a cylindrical plasma between plane electrodes we infer from the theoretical treatment of Tonks and Langmuir that $N\lambda^2$ lies between $1{\cdot}06 \times 10^{13}$ and $2{\cdot}12 \times 10^{13}$ according to the relative dimensions of the condenser plates and the diameter of the tube.

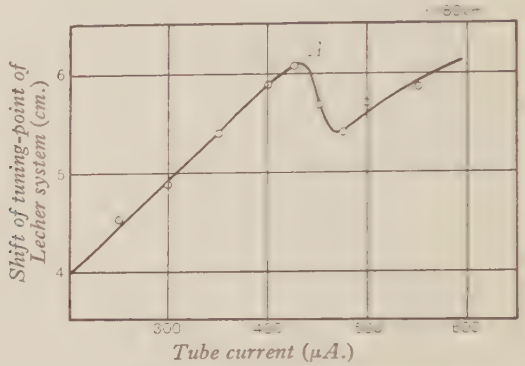

Fig. 4. Results relating to a wave-length of 80 cm.

For a wave-length of 80 cm. it will be seen that there is no sign of the quasi-resonance effects obtained by Gutton for the range of tube currents used. We believe that this was due to the fact that currents were not large enough to give the effect with this short wave-length. In order to check this point experiments were carried out with a wave-length of 370 cm. and the quasi-resonance effect was found. The electron concentration required to produce this effect was such that $N\lambda^2 = 1{\cdot}0 \times 10^{14}$. This agrees with the results of other experiments carried out in this laboratory which show that the value of $N\lambda^2$ is always greater for the resonance effect of Gutton than for the resonance due to plasmoidal oscillations. We believe, therefore, that the two effects are quite distinct.

§ 7. ACKNOWLEDGMENT

The experiments described in this paper were carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research.

DISCUSSION

The President asked how the amplitude of the oscillation executed by the electrons compared with the free path.

Authors' reply. Knowing the electric fields applied and the frequency of their alternation we can calculate the amplitude of the electronic vibrations. Neglecting friction, this is found to be about 2×10^{-4} cm., which is a small quantity compared with the mean free path.

SURFACE HEATING BY NEUTRALIZED POSITIVE RAYS BEFORE AND AFTER RETURN TO NORMAL STATE

By M. C. JOHNSON, M.A., D.Sc., Birmingham University

Received November 20, 1931. *Read and discussed February* 5, 1932

ABSTRACT. A nearly parallel beam of positive rays emerges through a cylindrical aperture in a cathode, and enters a space where the vacuum is kept high enough for gas collisions to be negligible. Experiments are carried out to decide whether the impact of neutralised atoms in the beam is able to heat a solid target to the same extent before and after their spontaneous return from excited to normal atomic state. This is done by investigating the disturbance of a bridge balance between two filaments accurately aligned across the beam at different distances along its path. With the aid of control experiments, and after elimination in the bridge of all effects common to the two wires, an excess heating is shown to occur in that filament which receives the larger proportion of atoms in excited states. The variation of this excess heating with the potential driving the discharge is found to be quantitatively in agreement with the variation of concentration of excited atoms at the different distances along the beam: this latter is calculated from Wien's experiments on the exponential decay of excited states along the path of neutralized positive rays.

§ 1. INTRODUCTION

When gas molecules strike a solid surface in a high vacuum, many kinds of energy exchange between the phases can take place, ranging from the very small transfer of kinetic energy accompanying specular reflection of molecules at a clean wire[1], to the violent destruction of an electrode surface by ionic bombardment, or the intense heating of a gas-solid interface at which a highly exothermic chemical reaction is taking place. In some previous studies I have described experiments illustrating two particular aspects of these energy exchanges: (*a*) the varying efficiency of thermal exchange when the solid is covered with different non-reacting layers of adsorbed gas[2], and (*b*) some conditions governing the liberation of energy when a hydrogen atom from the gas strikes and recombines with a hydrogen atom adsorbed on the solid[3]. An important though usually inaccessible variable in such investigations, independent of the kinetic energy of the impinging molecule, must be its state of internal energy, as specified by the quantum levels of its electrons. Some consequences of abnormal energy content of this kind are well known. For instance the concept of molecules which are activated, and thereby enabled to react at a surface, is familiar in chemistry. Recently several workers have shown that atoms in high quantum states can also cause the emission of electrons from solids on which they impinge, an energy

exchange which Oliphant[4] has investigated in detail. In a previous communication to this Society[5] I have described experiments in which mercury atoms, after excitation by absorption of certain radiations, cause liberation of gas from surfaces with which they collide. In view of such results it is desirable to devise direct thermal means of detecting any difference which may exist in the energy transferred by a gas molecule to a solid surface, according as the former is (*a*) in its normal state of minimum internal energy, or (*b*) possessed of excitation energy consequent on an electron having been raised to, or having been captured into, an outer orbit.

In the present paper we approach this problem by demonstrating a difference between the heating of a wire filament by impinging atoms before and after their spontaneous transition from higher to lower states of excitation; we use apparatus whose design aims at keeping constant all thermal exchanges between gas and solid phases, except those dependent on progressive de-excitation in the former.

Means for doing this are available from the classical experiments of Wien and his school, who studied optically a beam of positive rays entering a high vacuum, and traced the progress in spontaneous return of atoms to normal and other definite states. In our experiment we interrupt such a beam by two similar filaments, placed so that the principal difference between them is that one receives a considerable proportion of atoms before their return to normal and the other receives almost exclusively those whose return has been completed. We find that, after allowing for geometrical factors, the former filament acquires more heat from the rays than the latter, and that when control conditions are varied this excess varies in accordance with a law deducible from Wien's measured constant for the "decay" of excited states in a beam of neutral atoms. We conclude that either (*a*) excited atoms can communicate some of their internal energy as heat to a solid, or alternatively (*b*) possession of that energy renders them more than normally efficient in communicating to a target their kinetic energy or other source of heat such as energy of recombination.

We proceed to a quantitative treatment of such positive ray phenomena as constitute the mechanism of our experiment.

§ 2. THE EXPONENTIAL DECAY OF THE RATE OF ENERGY EMISSION FROM NEUTRALISED RAYS

When a beam of positive rays is allowed to escape into a highly evacuated chamber through a perforated cathode, it can be shown that a considerable proportion of the particles in the emerging stream are neutral. These have captured electrons close to the edge or side of the perforation, and may pass through more than one stage of excitation subsequently, but continue the high-velocity flight begun under the potential which had accelerated them when they were charged. Wien and others have shown that finite intervals of time elapse before these atoms regain their normal state of minimum internal energy; and since these intervals are commonly of the order of 10^{-8} sec., and the speed of the rays in an ordinary tube is of the order of 10^{8} cm./sec., the relative concentration of atoms in normal

and in still excited states will vary enormously over a length of a few centimetres along the path of the beam of rays. This variation is even roughly verifiable by eye, the luminosity accompanying de-excitation being intense just behind the cathode, decreasing over a short distance, and vanishing within a few centimetres, so long as the vacuum is high enough to eliminate the gas collisions which would allow the remaining ions to generate luminosity further along the tube. Such reorganization of the neutralized atom may take place by more than one process, but involves necessarily a loss of the difference between its excited energy E_1 and its normal energy E_2: there occurs either (*a*) the emission of a spectral line whose frequency is given by E_1 E_2

$$\nu = (E_1 - E_2)/h; \qquad \nu$$

or (*b*) a super-elastic collision in which $E_1 - E_2$ reappears as dissociation energy or kinetic energy in some molecule struck by the atom.

If, by the use of very fast pumps, the gas pressure behind the cathode is maintained much lower than that required to carry the discharge in front of the cathode, gas collisions may be neglected and the spontaneous process (*a*) predominates until the rays strike a solid surface. This spontaneous transition between quantum states has been shown to follow probability laws, which have been investigated in detail by Wien and his school. These laws are such that if the average time τ of duration of an excited state is given by τ

$$\tau = 1/2\alpha, \qquad \alpha$$

while the rays travel from the point of excitation along an x-axis with velocity v, the concentration N of atoms in still excited states at any point x is given by v N, x

$$N_x/N_0 = e^{-\kappa x} \qquad \kappa$$

$$= e^{-2\alpha x/v} \qquad \text{.....(1).}$$

By knowing the value of v and observing the decrement of the luminosity accompanying de-excitation for any given spectral line, Wien determined α and hence τ for various states of various atoms, using methods which he described to this Society in his Guthrie lecture in 1925.

The value of τ seems to be normally of one or other of two distinct orders of magnitude: (*a*) for many states of hydrogen and other common gases its value is between 10^{-7} and 10^{-9} sec.; (*b*) certain states of helium, mercury, and others are metastable, and terminate spontaneously only after 10^{-2} sec. or longer periods. In the experiments of Oliphant and others on the behaviour of excited atoms, use was made of metastable atoms which could travel long distances without de-excitation, but since we are here seeking a rapid variation of N_x, hydrogen is not unsuitable. The energy difference between atomic states of hydrogen most relevant to the present case is given by

$$E_1 - E_2 = 10{\cdot}15 \text{ electron-volts}$$

$$\doteqdot 235{,}000 \text{ cal./gm.-mol.}$$

This characterises transition from a 2-quantum to a 1-quantum state: by measurement of the exponential decay of Lyman lines Wien[6] determined for this transition

$$2\alpha = 14{\cdot}8 \times 10^7 \text{ sec}^{-1} \qquad \text{.....(2).}$$

In the present experiments we are concerned with the impact of the rays on targets placed at distances x_1, x_2, where

x_1, x_2

$$\left.\begin{aligned} x_1 &= 0{\cdot}9 \text{ cm.} \\ x_2 &= 2{\cdot}9 \text{ cm.} \end{aligned}\right| \qquad \text{.....(3).}$$

These distances are measured from the front face of the cathode, very close to which the majority of the atoms concerned start their transition by one of several possible mechanisms which need not be detailed here.

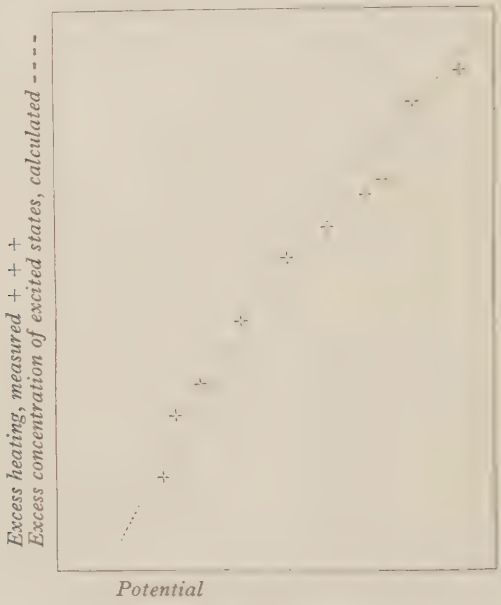

Fig. 1.

v would most accurately be obtained from the maximum of a curve of spectral-intensity-distribution across the Doppler-displaced line emitted, but to avoid violent disintegration of the delicate targets used it was necessary to keep the positive-ray current below the limit for accurate spectroscopic measurement. An average value of v can be approximately determined from

$$\tfrac{1}{2}mv^2 = e\bar{V} \qquad \text{.....(4),}$$

$e, m, \bar{V}$

where e and m are charge and mass of the proton and $\bar{V}$ is the effective potential corresponding to the velocity for a given Doppler effect. In a paper read some years ago before this Society I discussed the relation of $\bar{V}$ to V, the potential measured across the running tube; it was seen that

V

$$\bar{V} = \tfrac{1}{2}V \qquad \text{.....(5)}$$

can represent, at not too high potential, a fair approximation which we shall adopt here.

From equations (1, 2, 3, 4, 5) we calculate the proportion of atoms which still retain their excitation energy at the points x_1 and x_2 behind the cathode, for certain values of the accelerating potential measured across the tube.

V (volts):	2500	3000	4000	5000	6000	7000	8000
$e^{-2\alpha x_1/v}$:	0·067	·085	·118	·148	·174	·200	·223
$e^{-2\alpha x_2/v}$:	0·0003	·0004	·001	·002	·004	·005	·008

The dotted line in figure 1 represents the calculated variation of

$$[e^{-2\alpha x_1/v} - e^{-2\alpha x_2/v}]$$

with V.

This provides a means of interpreting any difference that our experiments may reveal between the extent to which targets at x_1 and x_2 are able to acquire heat by impact of atoms; since, if such difference is in fact due to difference in states of excitation, it should vary with V in the same manner as the above calculated quantity.

§ 3. APPARATUS

Figure 2 indicates the way by which it was arranged that hydrogen should flow continuously through the system, maintaining a gas-pressure sufficient to

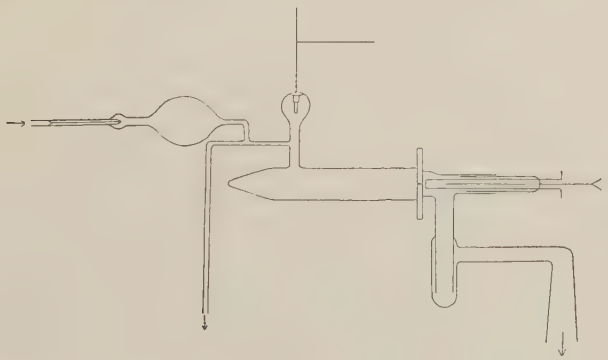

Fig. 2.

carry a discharge in the front portion of the tube while the region behind the cathode was continuously evacuated to about 10^{-5} mm. in order to eliminate gas collisions and so to allow the transitions between atomic states to be spontaneous except when atoms were striking the filaments. Steady admission of gas took place through a fine leak consisting of glass tubing drawn down on to asbestos fibre along its axis; this was found to be more constant in its conductance of hydrogen than the usual palladium valves, and, so far as could be determined spectroscopically, efficient as an impurity filter. The length and gauge of wire for

any required rate of flow was determined by preliminary experiments. An efficient liquid-air trap between the 3-stage steel vapour pump and the high-vacuum end of the tube was necessary, in view of the disintegration of tungsten filaments if accessible to mercury vapour, and was made large enough not to impede the rate of pumping seriously. The source of high potential was a large coil and rectifier: this is at a disadvantage compared with high-tension direct current, since the potential accelerating the ions fluctuates enormously around the value read on any instrument; but I was encouraged not to abandon the work for lack of direct current by the fact that some of the most accurate measurements of the exponential decay of hydrogen rays were carried out by Atkinson [7] with only an induction coil.

The rays were able to pass through the cathode by a cylindrical aperture, accurately bored with a fine drill, giving a conical beam of very small angle. At the distances x_1 and x_2, given above, were tungsten filaments perpendicular to the axis of the beam and to each other. These were rigidly supported on thick leads

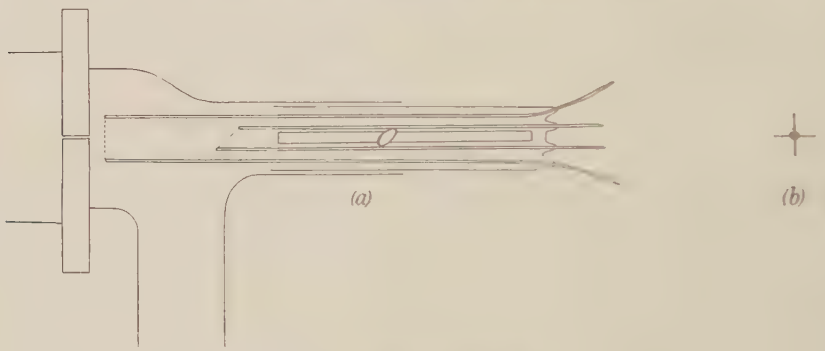

Fig. 3. Filament-mounting.

gripped between concentric glass cylinders and sealed into the system in such a way that no waxed surface was accessible to bombardment, figure 3 (*a*). The leads were carried by low-resistance mercury contacts to a bridge fitted with milliammeter and potentiometer means for checking the constancy of its electrical conditions. The resistances of the two filament systems were within 2 per cent of each other and remained so throughout. Care was taken not to heat the wires except in hydrogen, and to clean by glowing.

Since the positive-ray current was kept very small to minimise secular variations by disintegration of the filaments, their change of resistance due to heating by the impact of the rays was always small. Any differential heating of one in excess of the other was therefore a second-order quantity, and could be quite accurately studied in terms of the direct deflections of a reflecting galvanometer as the bridge balance between the two filaments was disturbed.

The constructional detail requiring most care was the alignment of the filaments relative to the beam of rays they were to interrupt. Unless they intercepted precisely known cross-sections of the beam it would not be possible to assume that

any disturbance of bridge-balance was due to the greater or lesser proportion of excited atoms striking one or the other. To check this accuracy of alignment a small mirror was mounted on the filament-supports, figure 3 (*a*), and a beam of light was projected along the axis of the discharge tube from the anode end: during final adjustment and sealings, and at any subsequent examination, the small circular spot of illumination provided by the cathode perforation could be observed in this mirror, and could be seen crossed accurately by the two filaments, as in figure 3 (*b*).

The following dimensions were adopted, and when transferred to a large-scale diagram were utilized to determine the extent to which the filament at x_1 screened that at x_2 from impact of the rays:

Diameter of cathode perforation:	0·075 ± ·003 cm.
Length of cathode perforation:	0·6 cm.
Diameter of filament wire:	0·015 cm.
Length of filament wire:	> 1 cm.

Hence at distances 0·9 and 2·9 cm. behind the front face of the cathode the filament-length ensured that each extended more than across the beam, whose divergence is calculable from the above dimensions. It is found that the calculated screening of x_2 by x_1 amounts to approximately 9 per cent.

§ 4. RESULTS

Each filament, when balanced separately against a constant resistance in the bridge, changed its temperature and resistance with any change of gas-pressure according to the normal Pirani effect. When, however, the two filaments were balanced against each other so that, to a first approximation, their Pirani effects cancelled, a disturbance of balance still occurred for any unidirectional net flow of gas through the perforation, and also, to a greater extent and in the opposite direction, for a stream of positive rays. The following experiments were carried out in the use of this disturbance for our purpose:

(*a*) To check the geometrical factor in the difference between the impact of rays on front and back filaments, calculated above as a 9 per cent screening effect, measurements were made of the galvanometer deflections accompanying the efflux of rarefied gas through the perforation into a high vacuum without any discharge. The beam of *atomstrahlen* thus striking the filaments was found to cool the filament at x_1 approximately 10 per cent more than that at x_2. (*b*) During discharge the stream of positive and neutralized rays was found to heat the filament at x_1 more than at x_2: the excess heating effect varied up to about 80 per cent according to the potential accelerating the rays, with comparatively small variation in the positive-ray current.

The measurements (*a*) and (*b*) were only susceptible of very limited accuracy, since they involved measuring the change of resistance of each wire separately, as well as the difference between the changes of resistance of the two when balanced. The latter we have referred to as a second-order effect compared with the former

as a first-order effect. It is only for the second-order effect that the bridge method serves to eliminate the great variety of undesired complications enumerated in § 5. Accordingly we place no weight on these preliminary measurements (*a*) and (*b*), except to prove that the excess heating of the front filament could not be accounted for merely by a geometrical effect of spread of beam, screening, or inaccuracy of alignment.

Hence there remains a large excess of heating by impacts on the front wire, which (*a*) and (*b*) show must be attributed to changes other than geometrical occurring in the beam between x_1 and x_2. We ascribe this to the excess concentration of still excited atoms, since such excess is both known to exist and is the only difference, other than geometrical, known to exist between x_1 and x_2.

(*c*) The quantitative correlation of impact heating with this concentration of normal and excited states was carried out by measuring the second-order effect, in terms of galvanometer deflections, for a sequence of different values of the potential across the tube. All those determinations whose reliability was checked by dependence on more than a single reading are plotted, in arbitrary units, upon the graph (+) of figure 1. This observed variation of the excess energy given by gas impacts to the front wire runs parallel, within the accuracy of the experiments, to the line already drawn to represent the calculated excess of atoms in the excited state. This parallelism only becomes a congruence if an additive constant is included; but owing to the necessary roughness of our method of obtaining v it is not safe to use this constant to correct x and so redetermine the point at which the rays were neutralized. In the absence of a more precisely known accelerating potential than is afforded by coil and electrostatic voltmeter, the investigation does not serve to do more than show the general agreement between the growth of excess heating and the growth of excess concentration of excited atoms.

§ 5. DISCUSSION OF RESULTS

Any interpretation of this heating accompanying de-excitation must be made in full consideration of the great variety of causes by which the temperature and resistance of a wire exposed to a gas may be changed. The following are the more important sources from which change of filament resistance may be expected under given conditions of the supply to it of electrical energy.

A. Fluctuations in the gaseous phase: (1) At low pressure, change of total gas pressure, or of partial pressure of differentially conducting components, heats or cools the wire. (2) Molecules of high potential energy may diffuse away from the wire, as in Langmuir's experiments with atomic hydrogen.

B. Secular alterations in the wire: (3) The accommodation coefficient, or fraction denoting efficiency of exchange of kinetic energy between gas and solid, is altered if the solid undergoes oxidation or other covering of the surface. (4) The area accessible to heat-conducting gas molecules is altered by recrystallisation or other secular changes in surface structure. (5) The volume resistivity of the wire alters if gas dissolves in or combines with the solid structure.

C. Temporary interaction of gas with wire: (6) Heat of adsorption may be

liberated. (7) Heat of reaction may be liberated if exothermic combination takes place between gas and solid, or between gas and adsorbed layer. (8) High-speed ions give up part of their kinetic energy to the wire on impact. (9) Impinging molecules in other than normal states may (possibly) communicate part of their internal energy to the wire as heat.

Processes (3), (4), (5) emphasise the importance of the precaution previously referred to in the treatment of filaments for this type of experiment. In a state of pressure equilibrium, or during isotropic changes of pressure, all causes will affect each of the two filaments equally, and so their effects are eliminated by the bridge arrangement used.

During non-isotropic pressure change, such as the efflux from the cathode perforation, the equality of effect on the two filaments is disturbed by the screening of one wire by the other. This was calculated in our case as 9 per cent, and measured, with respect to process (1) of the above list, as approximately 10 per cent in the rough first-order investigation.

The further excess heating of the front filament, which can only be ascribed to the greater concentration of excited atoms at the front filament, may be considered to act through more than one of the above-enumerated processes. There are two alternatives:

(*a*) The energy of de-excitation, representing the difference between the atomic state immediately after electron-capture or excitation and that after reorganisation of the atom into its normal state has been completed, may itself be partially transferred to vibrational energy of the atoms in the solid and reappear as heat, as in process (9). This would be analogous to the better known super-elastic collisions in the gaseous phase.

(*b*) Atoms before returning to normal state may be more efficient than normal atoms in liberating energy at the surface by processes (6), (7), or (8). If the forces of attraction between a neutral hydrogen atom and a tungsten surface depend on the electronic configuration of the former, the chance of adsorption and of recombination with already adsorbed atoms may be very different at the two wires, according as they receive greater or lesser proportions of atoms still in excited states. Similarly with regard to process (8), the transfer of kinetic energy from a fast atom, moving with a speed given by the accelerating potential when it was charged, depends on the mechanism of the collision: reflection coefficients and accommodation coefficients may be different for normal and excited atoms.

The relative amounts of energy available for transfer from impinging atom to solid are as follows:

(i) Kinetic energy in process (8).

$$\tfrac{1}{2}mv^2 = e\overline{V}$$

$$= 3{\cdot}2 \times 10^{-9} \text{ ergs per atom at 2000 volts.}$$

(ii) Heat of recombination in process (7).

$$100{,}000 \text{ cal./gm.-mol} = 6{\cdot}8 \times 10^{-12} \text{ ergs per atom}$$

$$= 4{\cdot}3 \text{ electron-volts.}$$

(iii) Heat of adsorption in process (6). Probably 10,000–20,000 cal./gm.-mol.

(iv) Energy emitted in de-excitation from nth orbit.

If $n = 2$, $E_1 - E_2 = 1{\cdot}6 \times 10^{-11}$ ergs per atom
$\div$ 10 electron volts.

If $n > 2$, $E_1 - E_2 > 10$ and $< 13{\cdot}6$ electron-volts.

It is clear from these data that kinetic energy of impact presents far the greater share of theoretically available energy at the gas-solid interface. This feature of the present investigation may be contrasted with the heating of a tungsten wire discussed in a previous paper[8]; in that case the kinetic energy of molecules was solely that of thermal agitation instead of being derived from large accelerating potentials, and the energy available was mainly the heat of recombination.

But any actual heating of the gas-solid interface depends not only on availability of energy but on efficiency of its transfer: the former we have stated as known, but little is known about the latter, so that it is impossible, in the present rudimentary stage of the kinetics of the interface, to resolve the above alternatives (*a*) and (*b*). The fact that the available energy is very largely kinetic, together with the fact that we find the excess heating due to de-excitation to be as great as 80 per cent, imposes, however, the following conditions on any interpretation of the alternatives:

(A) If the excess heating arises from a direct transfer of energy of de-excitation, the efficiency of the underlying physical mechanism must be large, compared with a very small efficiency of kinetic-energy transfer. It should be noticed that the high efficiencies sometimes attributed to the latter are generally taken from measurements of perpendicular incidence on a plane, and not, as here, on a convex surface of small radius, where impact is mainly oblique and probably inefficient as regards the exchange of energy.

(B) If the excess heating is an indirect consequence of excitation, the latter increasing the efficiency of such energy transfer as takes place by (i), (ii), (iii), the magnitude of (i) compared with the others indicates a greater likelihood that the mechanism of excess heating is an enhancement of the accommodation coefficient, or efficiency of transfer of purely kinetic energy at impact, for excited as compared with normal atoms. This would carry with it a modification of adsorbability and chemical activity, but the actual heating observed more probably represents part of the kinetic energy itself transferred with increased facility.

§ 6. CONCLUSION

The experiments establish that two filaments situated at different points along a beam of positive rays are differentially heated by the impinging beam. The control and screening experiments, and the use of a bridge method, limit the purely geometrical contribution to a verifiable 10 per cent difference, whereas the actual difference between the heating of the filaments rises to 80 per cent. The variation of the effect with the potential is shown to be quantitatively in accord with the

variation in the excess of excited atoms at one wire, calculable from Wien's experiments on the progressive return of neutral rays to normal state. We conclude that the greater part of the excess heating of one of the wires is controlled by the proportion of atoms which have not yet undergone spontaneous de-excitation. Hence the possession of energy of excitation in a neutralized atom enables it either to transfer some of that energy to the solid target, or else to increase the efficiency with which it transfers kinetic energy of impact. In either of these alternatives the beam of neutralized positive rays would exert an excess heating on the wire nearer to its origin, and this excess would vary with potential as we found it to vary, in accordance with the decay curves of excited states discovered by Wien.

§ 7. ACKNOWLEDGMENTS

I am indebted to Prof. S. W. J. Smith, F.R.S., whose kindness and generosity make possible this work, and also to Mr G. O. Harrison for his constructional skill and originality.

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DISCUSSION

Prof. E. V. Appleton. I imagine that the atomic stream issuing from the small orifice must contain some charged ions as well as the two varieties of neutralized atoms. It is known from the work of Holst and Oesterhuis, and also from the more recent experiments of Oliphant, that such ions can liberate secondary electrons from metal surfaces. The thermal profit-and-loss account of this process, in so far as the metal target is concerned, will depend on whether the emitted electrons are returned to the metal or whether they are collected by some other conductor which is maintained at a positive potential with respect to the target. I do not think that this effect could possibly upset Dr Johnson's conclusions (which seem to me very satisfactorily established) concerning the differential heating of the two filaments, since, with his symmetrical electrical circuit, the effects on both filaments would probably be identical. But if the experiments are pushed to a quantitatively further stage it would possibly have to be taken into account.

Author's reply: Undoubtedly there will be some positive ions left in the stream behind the cathode, though Oliphant has shown that their number may be small in some cases; the cooling of filaments when impact causes electron-emission will only occur if the surroundings are at high enough potential to draw off a considerable electron stream. If this occurs here it will affect both filaments alike, since hardly any change in the number of ions can take place between the two filaments at such low gas pressures. Neutralization needs a collision and will be very rare in the space of a couple of centimetres, whereas return of neutral atoms to ground state is spontaneous and needs no gas. Hence the effect mentioned will be among those eliminated by the bridge, as common to both wires.

ELECTROLYTIC WATER-TRANSPORT AND IONIC TRANSPORT NUMBERS

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Received November 15, 1931. *Read February* 5, 1932

ABSTRACT. This paper gives the results of determinations of the electrolytic water-transport per faraday in the case of copper sulphate solutions of concentrations ranging from normal to 1·8-normal. The parchment diaphragm method has been employed; and difficulties experienced owing to the effect of diaphragm-polarization have been surmounted by adopting a special experimental procedure. The electrolytic water-transport per faraday remains constant with increasing concentration of copper sulphate up to normal, as the author has shown in a former paper, but it decreases regularly with further increase in concentration. The probable factors contributing to this decrease are considered. The sequence in the values of the electrolytic water-transport per faraday corresponds with that in the values of the slope of the curve connecting the Hittorf transport number with the electrolyte concentration, but the corresponding values are not in numerical agreement as required by an expression proposed by Riesenfeld and Reinhold. This discrepancy is investigated by means of a more accurate expression derived by the author. The determinations of the electrolytic water-transport are employed to correct the values of the experimental Hittorf transport number.

§ 1. INTRODUCTION

The author, in a former paper*, has examined the relationship between the electrolytic water-transport and the transport numbers of the anion in the case of aqueous solutions of copper sulphate of normal and lower concentrations. It was found that the relationship could be expressed in terms of the slopes of the curves connecting the Hittorf transport number and the true transport number respectively with the electrolyte concentration; and there appeared to be a correspondence between the slope of the former curve and the electrolytic water-transport per faraday, both quantities remaining constant with increasing concentration of copper sulphate to normal.

At concentrations exceeding normal, the slope of the curve representing the Hittorf transport number decreases regularly with increasing concentration; and it seemed desirable to ascertain whether the electrolytic water-transport per faraday suffers a similar decrease. The present paper gives the results of an investigation into this question, the parchment diaphragm method being employed for the direct measurement of the electrolytic water-transport. The use of strong copper sulphate solutions, i.e. solutions of concentration greater than normal, was found to introduce difficulties owing to the effects of diaphragm-polarization, but an experimental procedure has been devised enabling satisfactory measurements to be made with solutions of concentration not exceeding 1·8-normal.

* H. C. Hepburn, *Proc. Phys. Soc.* **43**, 524 (1931).

§ 2. EXPERIMENTAL

The apparatus employed, which was similar to that described by the author in the former paper, consisted of two electrode chambers (one open to the air and the other closed) separated by a diaphragm of parchment paper. The liquid-transport across the diaphragm, when an electric field was applied at the electrodes, was determined, as in the previous work, by observing the movement of the liquid thread in a capillary tube attached to the closed electrode chamber.

The apparatus was immersed in an electrically heated water-bath with thermostatic control, the temperature of the bath being maintained within the limits $18 \pm 0{\cdot}1^{\circ}$ C. Moreover, to avoid thermometric effects, it was arranged that no heat should be supplied to the tank immediately before or during the course of the flow-measurements.

In the author's earlier measurements, which related to copper sulphate solutions of normal and lower concentrations, a potential difference of 20 V. was applied at the electrodes. The application of this voltage in the case of the more concentrated solutions of the present work was found to give rise to a considerable heating effect, the rate of liquid transport, as indicated by measurements made over consecutive lengths of the capillary tube, being less regular than in the case of the lower concentrations. It was therefore decided to adopt a lower working voltage.

Preliminary measurements with a potential difference of 4 V. applied at the electrodes showed that the current, after maintaining a constant value for a short period, slowly fell to a lower value, e.g. from 0·095 A. to 0·060 A. in the case of 1·4-normal copper sulphate solution. The period intervening between the establishment of the potential difference at the electrodes and the observed decrease in current value was found to decrease with increasing concentration. On reversing the direction of the current, the initial value was restored and was maintained for a period considerably in excess of the initial period.

In order to confirm that the effect described was not due to incomplete washing of the diaphragm, a further quantity of solution was allowed to flow through the diaphragm under a hydrostatic pressure head, and the measurement was repeated; a similar result was, however, obtained. It was evident, moreover, that the effect could not be ascribed to the copper electrodes employed, since no decrease in current value was observed when the diaphragm was removed from the apparatus. It appears probable from these results that the effect may be attributed to the establishment at the diaphragm of a polarizing counter-electromotive force which produces an additional apparent resistance in the circuit. In the analogous case of measurement of the conductivity of a collodion membrane in equilibrium with an electrolyte solution, A. A. Green, A. A. Weich and L. Michaelis* have avoided the production of a similar polarization effect by the use of an alternating current.

A similar diaphragm-polarization effect, obtained in the case of the electrolysis of a dilute solution divided by means of a diaphragm of collodion or of pig's bladder or the like, has been explained by A. Bethe and T. Toropoff† in terms of

* *J. Gen. Physiol.* **12**, 473 (1929).

† *Z. Phys. Chem.* **89**, 597 (1915).

the displacements in the ionic concentrations at the diaphragm boundary surfaces. Such concentration changes might be expected to produce a progressive building up of the polarization potential from the moment of establishing the external electric field; but the process, in the initial stages, appears to be a slow one in view of the sensibly steady values obtained for the current through the diaphragm in electro-endosmotic measurements with dilute solutions*. A similar action appears to operate in the case of the copper sulphate solutions employed in the present work, the slow beginning, or virtual time-lag, in the polarization process again being apparent. The effect of destroying the initial polarization potential by reversing the direction of the applied current is apparently to prolong the virtual time-lag in the establishment of a reversed polarization potential.

The decrease in current value referred to on page 268 was accompanied by a decrease in the magnitude of the liquid-transport; and it was only practicable, during the short period the current remained steady, to obtain an approximate measure of the liquid-transport. The current after reversal, however, maintained a steady value for a sufficient time to enable a measurement of liquid-transport to be made over 0·5 cm. of the capillary tube, but the reappearance of the polarization effect precluded satisfactory measurements in the case of solutions whose concentration exceeded 1·8-normal.

The rate of liquid-transport after current-reversal was found to be practically uniform whilst the current maintained a steady value and was in satisfactory agreement with the approximate initial measurement. The progressive displacements in the ionic concentrations at the diaphragm boundary surfaces, referred to above, thus appear to have no material effect on the present measurements.

Determinations of liquid-transport, following the procedure indicated in the preceding paragraphs, were carried out with the solutions in order of increasing concentration; and adjustment was made, as described in the former paper, for gravitational movement and for the thermometric action due to the heating effect of the current. The general procedure, preliminary to the measurements of liquid transport, was similar to that adopted in the former paper; and the initial direction of the applied electric field was selected so that the measured liquid-transport through the diaphragm, i.e. the liquid-transport after reversal of the applied field, was directed towards the closed electrode-chamber.

The direction of liquid-transport throughout the range of concentrations investigated was from anode to cathode.

§ 3. RESULTS AND CONCLUSIONS

The experimental results are given in table 1. $1/T_m$ (reciprocal seconds) is the reciprocal of the time of liquid-transport per cm. of the capillary tube, based upon measurements made over a length of 0·5 cm. of the tube, less the correction for the gravitational movement. The liquid-transport v_f in cm^3/faraday is calculated from the expression $[(1/T_m)(1/I_m)(0{\cdot}00973)(96{,}540)] - [6{\cdot}8]$, I_m being the mean current through the diaphragm in amperes, and 0·00973 the volume of the capillary

T_m

v_f

I_m

* H. C. Hepburn, *loc. cit.*

in cm³/cm. The deduction of 6·8 cm³ represents the correction for the heating
λ effect of the current. The values given for the specific conductivity λ have been obtained by large-scale graphical interpolation of the data of Kohlrausch.

Table 1.

Concentration of $CuSO_4$ (gm.-equiv./litre)	Mean current I_m (A.)	Specific conductivity λ (recip. ohms)	I_m/λ	Reciprocal of time of flow per cm. $1/T_m$	Liquid transport v_f (cm³/faraday)
1·0	—	—	—	—	30·6*
1·2	·0854	·0292	2·92	·003383	30·4
1·4	·0947	·0323	2·93	·003500	27·9
1·6	·1010	·0351	2·88	·003520	25·9
1·8	·1110	·0378	2·94	·003556	23·3

* Mean of two determinations with 6 V. applied at the electrodes. See H. C. Hepburn, *loc. cit.*

The electrolytic water-transport per faraday and its dependence on the electrolyte concentration. It will be observed from table 1 that the mean current I_m through the diaphragm is proportional, within close limits, to the specific conductivity λ of the solution. Control experiments showed also that the current value was only slightly increased when the parchment diaphragm was removed from the apparatus. The interposition of the parchment partition in the current path thus appears, during the short periods of measurement here adopted, to produce little change in the electrolytic transference of ions from one electrode chamber to the other.

The water-transport associated with this electrolytic transference of ions is given directly by v_f, table 1, since the specific (electro-endosmotic) effect of the parchment diaphragm may be neglected in the case of the high concentrations here considered†. The values of v_f decrease regularly with increasing concentration above normal, the rate of decrease from concentration 1·2-normal following a linear law. A similar relation to concentration has been found by J. Baborovsky and J. Velesek‡ in the case of solutions of certain alkali chlorides.

It was suggested in the former paper that the constant values obtained for v_f, the electrolytic water-transport per faraday, in the case of copper sulphate solutions of normal and lower concentrations, were probably the result of two antagonistic actions, (*a*) a decrease in the transport number of the cation with increasing concentration, and (*b*) a concurrent increase in the number of mols of water associated with one gram-equivalent of ions; the major effect under this head, since the resultant water-transport was directed towards the cathode, relating to the cations. The rate of decrease of v_f with increasing concentration from normal suggests, however, that the associated water referred to under (*b*) also diminishes as the saturation point is approached. This effect is possibly attributable to changes in the state of molecular aggregation of the solvent, e.g. breaking down of double

† See H. C. Hepburn, *loc. cit.*

‡ *Chem. Listy*, **22**, 265 (1928).

water molecules into single molecules, with decrease in the number of mols of water chemically bound to the ions*. Changes in the magnitudes of the inter-ionic forces and of the forces acting between the ions and the surrounding water molecules, with consequent variation in the number of water molecules carried along by the ions by means of viscous drag†, may also be of importance.

The values of v_f in table 1 relating to concentrations normal and 1·2-normal, viz. 30·6 cm.^{3} and 30·4 cm.^{3} respectively, are somewhat higher than the mean (29·3 cm.^{3}) of the "constant" values obtained in the former work over the concentration range 0·4-normal to normal. The variations involved, however, which appear to be within the limit of error in the former determinations of the current heating correction, have no material effect on the values of the true transport number‡, e.g. the value in the case of normal copper sulphate solution is changed from 0·666 to 0·664.

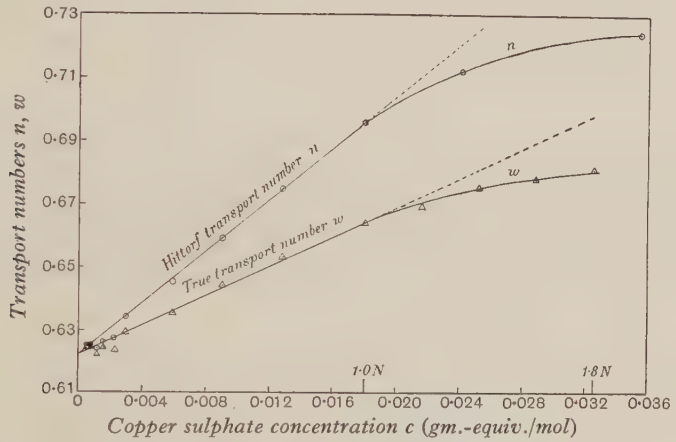

Fig. 1. Transport numbers plotted against concentration.

The relation between the electrolytic water-transport per faraday and the ionic transport numbers. The following equation, which connects the electrolytic water transport x in mols per faraday with the slope of the curve obtained by plotting the Hittorf transport number n against the electrolyte concentration c in equivalents per mol, has been proposed by E. H. Riesenfeld and B. Reinhold§, viz.

x

n, c

$$x = dn/dc \qquad \ldots\ldots(1).$$

The n/c curve appropriate to the case of copper sulphate solutions is given in figure 1. The values of n have been obtained from the data of H. Metalka‖ (concentrations 0·0212-normal to 0·1639-normal) and of W. Hittorf¶ (concentrations 0·327-normal to 1·96-normal)**. It will be observed that dn/dc remains constant

* See N. V. Sidgwick, *The Electronic Theory of Valency*, pp. 185 *et seq.* (1927).

† See H. C. Hepburn, *loc. cit.* p. 533.

‡ See page 272.

§ B. Reinhold, *Z. Phys. Chem.* **66**, 672 (1909).

‖ H. Jahn and collaborators, *Z. Phys. Chem.* **37**, 673 (1901).

¶ W. Hittorf, *Pogg. Ann.* **89**, 177 (1853).

** No data appear to be available for copper sulphate solutions of concentrations outside the range 0·0212-normal to 1·96-normal.

with increasing concentration to normal, but decreases regularly with further increase in concentration. There is a corresponding sequence in the values of x, the electrolytic water-transport per faraday, but the corresponding values of the two quantities are not in numerical agreement (see table 2), and $dn\,dc$ decreases more rapidly than x with increasing concentration from normal.

In order to investigate these discrepancies, it is convenient to examine the differential form of equation (1), arranged as an expression for x, viz.

$$x = dn/dc - dw/dc - c\,(dx/dc) \qquad \ldots\ldots(2).$$

It is easily seen that the simplified form proposed by E. H. Riesenfeld and
w B. Reinhold, viz. $x - dn/dc$, requires that w, the true transport number, and x should be independent of concentration. This condition is not fulfilled in the case of copper sulphate solutions. If x is alone independent of concentration, the term $c\,(dx/dc)$ vanishes, the resulting expression for x being applicable, as the author has pointed out in his former paper, to the case of copper sulphate solutions of normal and lower concentrations.

Equation (2) provides no independent basis for testing the experimental values of x, but it appears to be a matter of interest to trace the relative importance of the three terms on the right hand side of the equation as the concentration is increased from normal. Values of the three terms in question, which have been obtained by drawing tangents to the corresponding curves, are given in table 2. It will be seen that the third term is predominant in the case of the highest concentration.

Table 2.

Concentration c of $CuSO_4$ (gm.-equiv./mol)	Electrolytic water-transport x* (mol/faraday)	dn/dc	dw/dc	$c\,(dx/dc)$
·01806 (1·0 N)	1·70	4·1	2·4	0·0
·02166 (1·2 N)	1·69	2·6	1·4	− 0·5
·02528 (1·4 N)	1·55	1·9	1·2	− 0·9
·02890 (1·6 N)	1·44	1·2	0·9	− 1·1
·03256 (1·8 N)	1·29	0·5	0·4	− 1·2

* $x = v_f/18{\cdot}02$ (see table 1 for values of v_f).

Determination of true transport number. The following relation between the electrolytic water-transport and the ionic transport numbers, appropriate to the case of copper sulphate solutions, has been deduced by E. H. Riesenfeld and B. Reinhold†, viz.

$$w = n - cx \qquad \ldots\ldots(3).$$

Here w is the true transport number, n the experimental Hittorf transport number, c the electrolyte concentration in equivalents per mol, and x the electrolytic water-transport in mols per faraday. The symbols w, n refer to the anion.

The values given in table 3 for the true transport number w, in the case of

† *Loc. cit.*

copper sulphate solutions of concentrations ranging from normal to 1·8-normal, have been computed by means of this equation from the present experimental results for the electrolytic water-transport per faraday.

Table 3.

Concentration c of $CuSO_4$ (gm.-equiv./mol)	Hittorf transport number n	True transport number w
·01806 (1·0 N)	·695	·664
·02166 (1·2 N)	·706	·669
·02528 (1·4 N)	·714	·675
·02890 (1·6 N)	·720	·678
·03256 (1·8 N)	·723	·681

The values of the Hittorf number n have been obtained by large-scale graphical interpolation from the data of W. Hittorf*. The solution-densities required to compute the concentration values in equivalents per mol were specially determined by the author.

It will be seen from table 3 and from the figure that both the Hittorf transport number n and the true transport number w increase regularly with increasing concentration. The rates of increase, however (see table 2), diminish with increasing concentration; and it seems probable that the values of n and w at concentrations exceeding 1·8-normal suffer little variation.

§ 4. ACKNOWLEDGMENT

The author desires to thank Prof. A. Griffiths for facilities provided and for the interest he has shown in this investigation.

* *Loc. cit.*

ON THE MAGNETIC SUSCEPTIBILITIES OF SOME NICKEL COMPOUNDS

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Received December 1, 1931. *Revised January* 13, 1932. *Read February* 5, 1932

ABSTRACT. The susceptibilities of a number of compounds of nickel in the solid state have been measured at room temperature. The atomic susceptibility of combined nickel is found to remain constant, except in the cases of the anhydrous cyanide and of dioxime compounds. Some of the latter are diamagnetic.

§ 1. INTRODUCTION

Some time ago it was suggested to me by Prof. C. H. Lees that the para- and diamagnetic effects in the molecule of a nickel compound might be capable of being distinguished by a study of the temperature susceptibility relation, and that in particular it might be possible, in the extreme case of a combination of the nickel atom with a strongly diamagnetic acidic radical, to find one effect or the other predominating, according to temperature, so that at a certain critical temperature the sign of the susceptibility would be reversed.

An investigation on these lines has been begun with a series of measurements of the susceptibilities of various nickel compounds at room temperatures, in order to detect any in which the diamagnetism of the acidic radical contributes substantially to the net susceptibility, and the present paper gives an account of these measurements.

§ 2. METHOD

The method used was of the non-uniform-field type, the electromagnet being fitted with specially designed pole-pieces to give a field of such configuration that considerably more latitude than usual was possible in setting different specimens to the same part of the field—this setting constituting the greatest difficulty and principal source of error in the usual non-uniform-field method. The majority of the measurements were made with an apparatus which has already been described*.

For subsequent work on more weakly magnetic substances (cyanides and dioximes) it was necessary to increase the sensitivity of the apparatus. This could have been effected quite simply by fitting a suspension of smaller restoring couple in the torsion balance, but advantage was taken of the opportunity to rebuild the apparatus with several improvements in matters of detail.

* *Proc. Phys. Soc.* **42**, 251 (1930).

The field. As a result of a more extended investigation of the problem of pole-piece design* it became possible to produce a field in which the force exerted on a small para- or diamagnetic body remained constant over a much wider region, so that even the rough setting to a standard position used with the earlier apparatus became unnecessary. The way in which the force exerted on the specimen varied with position in the interpole gap is shown by the curve of figure 1. The pole-pieces used were those described as giving the distribution of figure 10 (*d*) in the paper just referred to, but they were used with a slightly smaller gap in order to flatten out that curve to the more suitable form shown in the accompanying figure 1.

The torsion balance. In place of the simple glass T-tube originally used to contain the torsion balance, a somewhat more elaborate arrangement was built up in order to make the balance more accessible. Glass tubes *G*, figure 2, were cemented

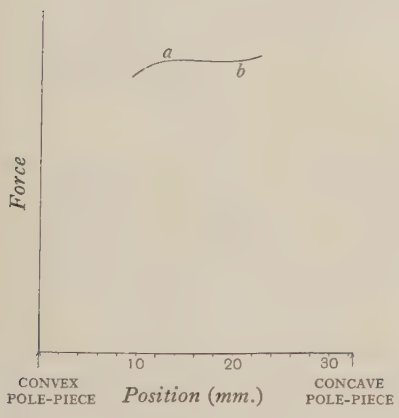

Fig. 1. Distribution of force across the interpole gap.

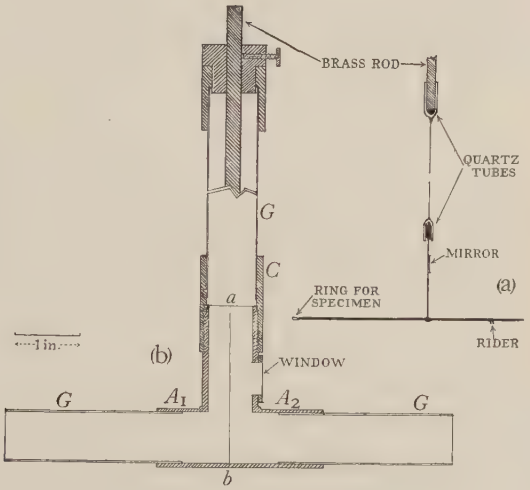

Fig. 2. The torsion balance. (*a*) The suspended system; (*b*) the T-tube.

into a brass T-piece split into two parts A_1, A_2 by a cut along *ab*, over which was screwed a collar *C* carrying the vertical glass tube. The whole was held firmly together when *C* was screwed up, but could be dismantled readily by unscrewing. The two ends of the horizontal tube were closed, as before, by paper caps with glass windows, and a torsion head was fitted to the upper end of the vertical arm.

The balance itself consisted of a rod of specially prepared glass of low susceptibility, to the centre of which was attached a support of copper wire carrying also a galvanometer mirror. The upper end of this wire was cemented into a short length of quartz tube to which the suspending quartz fibre was fused. The upper end of the fibre was similarly fused to a quartz tube which was cemented to a brass rod passing through the torsion head. The specimen was carried on a small wire loop at the end of the arm, and small differences in the weights of different specimens were balanced by a light rider.

* *Proc. Phys. Soc.* **43**, 383 (1931).

Deflections of the system were observed by reflection of a beam of light to a scale at a distance of 2 m. The height of the scale was such that the light spot fell upon it when the rider had been adjusted to bring the specimen to the correct height, i.e. to the axis of symmetry of the field. The diameter of the T-tube, and its position in the field, were so chosen that the specimen was confined to the region *ab*, figure 1, of the field. Thus the only adjustment necessary after a specimen had been placed in the balance was to shift the rider until the spot of light appeared on the scale, showing that the specimen occupied a position on the axis of symmetry of the field.

Since the apparatus consists essentially of an electrically isolated system suspended within a glass tube, electrostatic forces between the fixed and suspended systems might be expected, but were never detected. This was doubtless due to the fact that the apparatus was installed in a very damp basement laboratory, and the atmosphere was always sufficiently humid to prevent the accumulation of electrostatic charges.

§ 3. MATERIALS

The compounds used were in most cases commercial products of the purest grade available. In the case of some of the more unusual compounds, the preparations were made in the laboratory. For this preliminary survey the salts were not subjected to any further purification. The following particulars refer to the salts for which results are given in table 1.

Nickel sulphate. A specially pure sample of the heptahydrated sulphate was used.

Nickel citrate. Obtained in a high state of purity as slightly dried $Ni_3(C_6H_5O_7)_2.14H_2O$, for which the theoretical percentage of nickel is 21·8. The actual percentage was found by analysis to be 22·1.

Nickel potassium sulphate. This was also slightly dehydrated, the percentage of nickel being found to be 14·7. The theoretical value for $NiSO_4K_2SO_4.7H_2O$ is 14·2 per cent.

Nickel benzoate. $(C_6H_5COO)_2Ni.3H_2O$, checked by analysis.

Nickel formate. Certified by the manufacturers as 78 per cent anhydrous $Ni(HCOO)_2$. This corresponds to a composition intermediate between a di- and a trihydrate.

Nickel cyanide. A light green powder, found by analysis to contain 40·32 per cent nickel and about 25 per cent water. This corresponds closely to a composition $Ni(CN)_2.2H_2O$.

Nickel borate. Found by analysis to contain 32·9 per cent NiO and 36·4 per cent B_2O_3. This does not correspond to any exact composition, and it is probable that the product consisted of a mixture of borates, of which a number are known.

Nickel ammonio-sulphate. A bright blue powder, found by analysis to contain 21·2 per cent nickel. A blue compound having the composition $NiSO_4.4NH_3.2H_2O$

is known; it contains 22·7 per cent Ni, and the closeness of the theoretical figure to the observed percentage suggests that the preparation consisted mainly of this compound.

§ 4. EXPRESSION OF RESULTS

Suppose a compound to consist of x per cent nickel, y per cent of an acidic radical, and $(100 - x + y)$ per cent water, whose mass susceptibilities in the combined state are χ_x, χ_y, and χ_w respectively. Then, provided that an additive law is followed, the mass susceptibility χ of the compound will be given by

x

y

χ_x, χ_y, χ_w

$$100\chi = x\chi_x + y\chi_y + (100 - x - y)\chi_w \quad \text{.....(1).}$$

Investigations on simple salts have already shown that in the case of most simple compounds such a law is followed, and that the last two terms, in the case of salts containing strongly paramagnetic radicals such as nickel, are negligible in comparison with the first.

Thus, as a close approximation, we may write

$$100\chi = x\chi_x,$$

$$\chi_x = 100\chi/x,$$

or, for the gram-atomic susceptibility, χ_A, of the combined nickel,

$$\chi_A = 5869\chi/x \quad \text{.....(2).}$$

From the results of the measurements, χ_A was evaluated according to expression (2), x having been determined by a chemical analysis. The majority of simple salts gave a nearly uniform value for χ_A, the gram-atomic susceptibility of combined nickel plus the small correcting terms for acidic radical and water. When a divergent value was obtained, the divergence indicated either (*a*) that the contribution of the acidic radical or of the combined water was not negligible in comparison with that of the combined nickel; or (*b*) that the constituents entered into such intimate union that the additive law did not hold; or (*c*) that the effective susceptibility of the combined nickel had a new value.

The magnetic moments have also been expressed approximately in terms of Weiss magnetons by assuming a Curie law ($\chi = C/T$) to be followed. Since, however, solid salts more usually follow a Curie-Weiss law,

$$\chi = C/(T - \theta),$$

these p values* have but little value as such; but the results are useful inasmuch as the fact that the values deduced, with one exception, lie between 15·9 and 16·3 (see table 1) may be taken as an indication that the values of θ for the substances investigated are small.

p

* p is defined as the moment of the gram-molecule, expressed as a multiple of the Weiss unit, 1126 c.g.s.

The observations gave relative susceptibilities. For the purpose of this work they are converted into absolute susceptibilities with sufficient accuracy by assuming Jackson's value for the susceptibility of nickel sulphate—viz. $16{\cdot}0 \times 10^{-6}$ at 292·2° K.*

§ 5. RESULTS

Table 1 gives results for a number of materials which were known to be of reliable purity, and the compositions of which were known with accuracy, as has already been explained.

Table 1.

Salt	Formula	$\chi.10^6$	Ni (%)	$\chi_A.10^4$	p
Nickel formate	$Ni(HCOO)_2 + x.H_2O$	23·3	30·8	44·4	16·0
Nickel cyanide	$Ni(CN)_2.2H_2O$	21·0	40·3	30·6	13·3
Nickel borate	?	19·4	25·8	44·0	15·9
Nickel citrate	$Ni_3(C_6H_5O_7)_2 . 14H_2O$	17·5	22·1	46·5	16·3
Nickel sulphate	$NiSO_4 . 7H_2O$	16·0	20·9	44·9	16·1
Nickel ammonio-sulphate	$NiSO_4 . 4NH_3 . 2H_2O$?	15·9	21·2	44·0	15·9
Nickel benzoate	$Ni(C_6H_5COO)_2 . 3H_2O$	12·7	16·5	45·0	16·1
Nickel potassium sulphate	$NiSO_4K_2SO_4 . 7H_2O$	11·1	14·7	44·3	16·0

Although this list includes compounds of various types—mainly with fairly complex organic radicals, the deduced atomic susceptibility of the combined nickel remains nearly constant with a single exception in the case of the cyanide. We thus have strong evidence that the susceptibility of these compounds is due almost entirely to the nickel. The cyanide is dealt with in the next paragraph. With the single exception of the citrate, the compounds listed are all salts of dibasic acids. The citrate, with three nickel atoms to the molecule, gives a value for the atomic susceptibility which is definitely higher than that deduced from measurements on the other salts. The phosphate, also with three nickel atoms to the molecule, gives a similar value, but in this case the result is more uncertain: see table 2.

In table 2, results are given for some compounds of more doubtful composition.

Table 2.

Salt	Formula assumed	$\chi.10^6$	Ni (%)	$\chi_A.10^4$
Nickel phosphate	$Ni_3(PO_4)_2 . 7H_2O$	28·2	35·8	46·2
Nickel acetate	$Ni(C_2H_3O_2)_2 . 4H_2O$	17·8	23·6	44·3
Nickel ammonium sulphate	$NiSO_4(NH_4)_2SO_4 . 6H_2O$	11·0	14·9	43·3
Nickel cyanide	—	15·9	—	—
Nickel ferricyanide	—	28·4	—	—
Nickel ferrocyanide	—	11·9	—	—
Nickel fluoride	—	25·9	—	—
Nickel oxalate	—	18·9	—	—
Nickel carbonate	—	32·9	—	—
Nickel chromate	—	30·3	—	—

* *Phil. Trans.* A, **224**, 1 (1923).

In the case of the first three compounds, the formula given was known to be correct apart from some uncertainty as to the exact water-content. The remainder were probably in most cases mixtures of different hydrates, or of normal and basic salts.

Nickel cyanide. The results given in table 1 definitely indicate some anomaly in the susceptibility of the cyanide, and a more detailed investigation of this compound was therefore decided upon. Since the observation of this anomaly*, Bose† has called attention to the low susceptibility of nickel cyanide, and suggests that in the completely anhydrous state the compound will be found to be diamagnetic.

In the first instance, three samples of commercial "pure" nickel cyanide have been investigated. On dehydrating at 180 to 200° C., each sample is reduced to the brick-coloured anhydrous cyanide, with a considerable reduction in susceptibility. The susceptibility of the dehydrated salt appears to be a constant, characteristic of each sample; thus the cyanide for which results are given in table 1 always lost 25 per cent in weight, the susceptibility falling to about 15×10^{-6}; that quoted in table 2 lost 40 per cent, with a reduction of the susceptibility to 8×10^{-6}. The third sample, dehydrated at from 180 to 200° C., and cooled over phosphorus pentoxide, gave the lowest susceptibility so far observed, namely $+ 3 \times 10^{-6}$.

The observations are not yet sufficiently complete to permit definite conclusions to be drawn, but the results are not incompatible with the theory that the pure anhydrous salt is diamagnetic, since the normal method of preparation of the compound is very liable to introduce impurities, chiefly double cyanides. The results would be explained if the different specimens contained different proportions of a paramagnetic impurity.

Experiments are now in progress with nickel cyanide so prepared as to prevent the introduction of such impurities.

Observations on the ferri- and ferrocyanide are listed in table 2; it was difficult to obtain consistent results, especially in the case of the ferricyanide, and the values given must be regarded as approximate only.

Dioxime compounds. The chemical analysis which had to be carried out during the work involved the preparation of nickel dimethylglyoxime in a high state of purity, and measurements of the susceptibility of this, one of the most complex compounds available, were made. It was found to be feebly diamagnetic. The similar nickel α-benzil dioxime compound was likewise found to be diamagnetic, but one prepared from methylpropyl ketone was slightly paramagnetic. The susceptibility in each case was of the order 10^{-7}; more precise measurements will be made when the apparatus has been modified to permit of a study of susceptibilities at various temperatures.

These are the only nickel compounds which the work has so far shown to be diamagnetic. It is interesting to note that, of the simple salts examined, the brick-coloured anhydrous cyanide is practically the only one not possessing the green or yellow colour characteristic of most nickel salts, and it is the only one with an anomalous susceptibility. On hydration, the compound becomes green, and the

* The measurements were made in 1928.

† *Nature*, **125**, 708 (1930).

susceptibility approaches a normal value. The composition of the red chromate was not known with sufficient accuracy to allow the atomic susceptibility to be deduced. The more complex red and orange dioxime compounds also show anomalous susceptibilities.

§ 6. ACKNOWLEDGMENTS

This work has been carried out at East London College, with the aid of grants from H.M. Department of Scientific and Industrial Research. My best thanks are tendered to Prof. C. H. Lees and Prof. H. R. Robinson for their advice and assistance.

ELECTRONS AND LIGHT QUANTA

By Sir AMBROSE FLEMING, F.R.S., Emeritus Professor of Electrical Engineering in the University of London

Received December 18, 1931. *Read and discussed February* 19, 1932

ABSTRACT. The question whether electrons moving with or against a stream of photons are accelerated or retarded by the momentum of the latter is considered. A study based on known physical constants suggests that the magnitude of such an effect should be measurable in the case of strong sunlight and *a fortiori* of X-rays, but an experimental test has yielded negative results. The conclusion is reached that either photons do not exist as defined mass particles during the transmission of light-energy, or else that the apparent area covered by photons in a beam of radiation or by electrons in an electronic current is very small in comparison with the cross-section of the beam or current.

§ 1. INTRODUCTION

It is well known that whilst many optical phenomena can be explained by a wave theory of Light in which the energy is distributed without discontinuity over the wave front, there are other phenomena such as photo-electric effects, the ionization of gases, and also the distribution of energy along the spectrum that seem to demand a quantum theory in which radiant energy is assumed to be emitted or absorbed by atoms in certain definite units.

The effects of interference and diffraction are perfectly explainable in terms of a wave theory in which the oscillating vectors of the light wave, which in accordance with Maxwell's theory are taken to be respectively electric and magnetic forces or fluxes, are at right angles to each other, in step as regards phase, and both normal to the direction of propagation of the wave. The wave-energy or light-intensity is then capable of infinitely gradual variation, and varies as the square of the amplitude.

On the other hand, all those electro-optic phenomena in which electrons enter or leave atoms in exchange for radiation are not explainable, apparently, unless we assume that the light energy is absorbed and emitted in quanta such that the energy of each quantum or photon is numerically equal to the product $h\nu$ where ν is the wave frequency and h is Planck's constant of action, the best value of which is $6{\cdot}5543 \times 10^{-27}$ erg-sec.

Moreover, the pure undulatory theory has never been able to explain the distribution of energy in the spectrum and the fact that it reaches a maximum value for some wave-length intermediate between very long and very short waves in the case of the radiation of a black body in a state of incandescence. The theory of light quanta alone has given an explanation of this fact and Max Planck has deduced a well-known formula for the energy density of radiation of a black body expressed

in terms of wave-length or frequency. On this theory the energy-density of radiation can only increase or decrease by steps or finite units and the intensity is expressed by the number of light-quanta per cm^3

Einstein put forward in 1905 the suggestion that the energy of radiation whilst being transmitted is concentrated in certain packets or quanta each of energy $h\nu$ and that these travel as such through space with the velocity of light. According to this view a beam of light more resembles a shower of rain than a pure wave motion. Just as the rain consists of discrete drops of water so the light is thought to consist of drops of energy called photons. But this view is perfectly inconsistent with the known facts of interference and diffraction.

G. I. Taylor and also G. P. Thomson have shown that even when light is so feeble that 2000 hours of exposure of a sensitive photographic plate was necessary to secure with it a photograph, it was possible with such feeble light to photograph diffraction-patterns quite sharply which never could be seen directly by the eye since the intensity was so low that only about 1 quantum or photon was contained in 10,000 cm^3.* It is impossible to understand how interference can take place unless at least two quanta arrive simultaneously at the same point by different paths.

Hence an eminent physicist, the late Dr H. A. Lorentz, has said, "It must I think be taken for granted that the quanta can have no individual and permanent existence in the ether, that they cannot be regarded as accumulations of energy in certain minute spaces flying about with the speed of light." In other words, the quanta do not travel through space as such and cannot be regarded as constant spatial entities like electrons or protons.

Seeing then that neither a pure wave theory nor a pure quantum theory of light will explain all known optical phenomena, a compromise has been effected by the assumption that both waves and photons exist, but that the photons carry the energy and the waves guide the photons so that the number of photons per cm^3 is proportional to the energy of the light. It may be objected that a wave conveying no energy is an impossible conception, but we might evade this difficulty by the assumption that the energy of the true wave is very small compared with the energy concentrated in the photons. If then a beam of light can in any way be regarded as a stream of photons or light quanta each having energy and mass, and if the wave energy is electromagnetic in nature, the question arises whether a stream of electrons moving along a beam of light would have their velocity increased or diminished according as they moved with or against the direction of propagation of the light.

§ 2. THEORETICAL CONSIDERATIONS

As will be mentioned presently this question has been tested experimentally, but as a first step it will be of advantage to inquire what theory has to say about the matter.

* See J. H. Jeans, *Report on Radiation and the Quantum theory*, p. 80 (Phys. Soc. 1924).

Planck's formula for the energy-density E_ν of radiation of a black body lying between the frequency limits ν and $\nu + \delta\nu$ is

$$E_\nu = u_\nu d\nu = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} d\nu \qquad \ldots\ldots(1),$$

where $c = 3 \times 10^{10}$ cm./sec. and is the velocity of light, $h = 6{\cdot}55 \times 10^{-27}$, T is the absolute temperature of the black radiator, and k is the gas constant per molecule or $1{\cdot}37 \times 10^{-16}$. Suppose then we apply this formula to the most intense light available, namely brilliant tropical sunlight.

The solar photosphere may be taken to be a black-body radiator at a temperature of about 6000° K. The temperature varies from 6760° K. at the centre of the solar disc to 5400° K. at the edge. The wave-length λ_m corresponding to the maximum energy-density of the solar spectrum is 4700×10^{-8} cm. by observation*.

By Wien's law the product of the absolute temperature of the radiator and the wave-length of maximum energy-density must be equal to 0·2940, or $T\lambda_m$, so that $T = 0{\cdot}294/\lambda_m$. Hence $T = 6254°$ K. which is within the limits of observation.

We have next to settle the value of $d\nu$ numerically. Let us take a range of frequency from about two octaves below the red end of the spectrum, namely $100 \times 10^{12} \sim$, to about an octave beyond the violet end or to $1000 \times 10^{12} \sim$. The difference between these extreme values is 900×10^{12}. If we suppose this spectrum cut up into a million slices, each slice may be considered to be approximately constant in frequency and hence $d\nu = 9 \times 10^8 = 10^9$ nearly.

Supposing then we take ten equidistant values of the frequency ν from 10^{14} to 10^{15} covering the thermal spectrum, and assuming that $d\nu = 10^9$, calculate by Planck's formula (1) the corresponding energy-density for each of these frequencies. I find by trial that when the value of T is taken as 6000° K., so that $kT = 8{\cdot}22 \times 10^{-13}$, the frequency of the maximum energy-density of sunlight would fall at a frequency of 3×10^{14} instead of at 6×10^{14} as it actually does.

Hence I infer that for temperatures as high as 6000° K. the temperature T enters into the exponential function in Planck's formula at a power slightly higher than the first power. I find by trial that to comply with Wien's law we must take kT in Planck's formula to have a value of 13×10^{-13} for bright sunlight. Inserting this value and then calculating the energy-density of radiation for the stated frequencies we have the results given in table 1. It will be seen that the maximum energy-density then falls, as it should do for sunlight, at a frequency of 6×10^{14}.

Also since the energy of each photon or quantum is $h\nu$, if we divide out Planck's expression for the energy-density by $h\nu$ we shall have the value as given in the last column of table 1 for the number of photons or quanta per cm.^{3} for each frequency, on the assumption that these quanta or photons actually exist as such in the transmitted radiation. The values of the energy and photon-density for sunlight are plotted out in terms of the frequency in figure 1, and are taken

* See *Handbuch der Astrophysik*, 4, 30.

from the calculated values at each frequency as given in table 1. It will be seen that the energy-density values rise to a maximum at the proper frequency and that the photon-density also rises to a maximum but not at the same frequency.

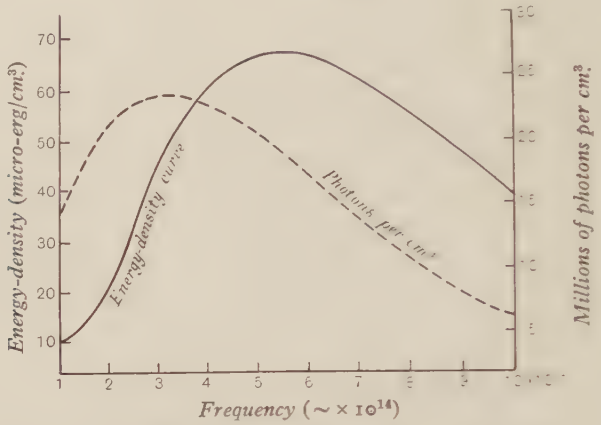

Fig. 1. Planck's energy-density curve for sunlight.

Table 1. Energy-density and photon-density for sunlight.

$T = 6000°$ K., $kT = 13 \times 10^{-13}$, $dv = 10^9$, $h = 6{\cdot}55 \times 10^{-27}$ in Planck's formula.

Frequency of radiation v $\sim \times 10^{12}$	v^3 $\sim^3 \times 10^{42}$	hv (c.g.s. units $\times 10^{-13}$)	hv/kT	$\epsilon^{hv/kT}$ or x	Energy-density (ergs cm³ $\times 10^{-6}$)	Photons per cm³ ($\times 10^6$)
100	1	6·55	0·5	1·648	9	13·8
200	8	13·1	1·0	2·718	20	21·4
300	27	19·65	1·508	4·518	46	23·4
400	64	26·2	2·01	7·463	59·4	22·6
500	128	32·75	2·52	12·431	65·6	20·0
600	216	39·3	3·02	20·492	66·7	17·0
700	343	45·9	3·53	34·125	62·1	13·5
800	512	52·4	4·03	56·264	55·5	10·6
900	729	59·0	4·54	93·705	47·2	8·0
1000	1000	65·5	5·04	154·471	39·2	16·0
				Mean value:	$47{\cdot}87 \times 10^{-6}$	$15{\cdot}7 \times 10^6$

It will be seen from table 1 that the average energy-density of sunlight is near to 48 micro-ergs per cm³ and the average number of photons is near to 15 million per cm³. This value, obtained as the mean of 10 equidistant ordinates, must be somewhat less than the true mean value.

Maxwell has shown* that the number which denotes the energy-density of radiation denotes also the pressure of radiation per square unit. In the experiments on light-pressure made in 1903 by Nichols and Hull† these observers found that

* *Treatise on Electricity and Magnetism*, **11**, 401 (2nd ed.).

† *Proc. Amer. Acad. of Arts and Sci.* **38**, 539 (1903).

the light-pressure did agree with the energy-density to within 1 per cent, and that this light-pressure for sunlight would be about 50 microdynes/cm².

Again, we have numerous measurements of the solar constant, that is the heat in calories per minute produced when full sunlight falls normally on 1 cm² of a black surface. This varies from time to time, but a good average value is 1·94 cal./cm²-min. Translating this into ergs per second we find it to be 1·36 million ergs/sec. Hence dividing by 3×10^{10} we have the mean energy-density of sunlight as 45 micro-ergs/cm², which is in fair agreement with our calculated value of 48 micro-ergs from Planck's formula. This value derived from the solar constant may however also be too low, as correction for atmospheric absorption is difficult.

Furthermore we can check this result by the observed values of Stefan's constant. Stefan's law is that the radiation per cm² of a black body is proportional to the fourth power of the absolute temperature multiplied by a constant, and the mean of 12 determinations of this constant σ as given by Fritz Reiche* is $5{\cdot}8 \times 10^{-5}$ ergs/cm²-sec. σ

The solar surface-temperature is 6000° K. and hence $T^4 = 13 \times 10^{14}$ and $\sigma = 5{\cdot}8 \times 10^{-5}$. Therefore $\sigma T^4 = 75 \times 10^9$. Now the radius of the earth's orbit is $14{,}945 \times 10^9$ cm. and the radius of the sun is $69{\cdot}5 \times 10^9$ cm. The ratio is 215 to 1 and the square of that ratio is 46,225. The radiation from the sun at its surface is thus 75×10^9 erg/cm²-sec. and dividing this by 46,225 and again by 3×10^{10} we have for the mean energy-density of solar radiation at mean earth distance 54 micro-ergs, which is not far from the results obtained from Planck's equation and from those of the measurements of light-pressure.

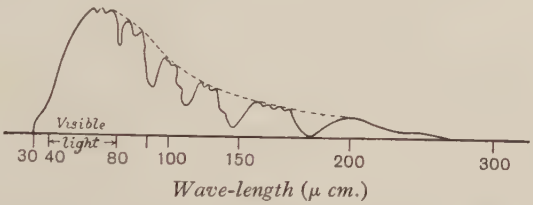

Fig. 2. Bolometer curve for bright sunlight with energy-density plotted in terms of wave-length.

A fourth method by which we can obtain a value for the mean energy-density of sunlight is the integration of the bolometer curve of sunlight. When a bolometer wire is passed along a solar spectrum the readings at every stage give us an ordinate of the radiation-energy curve, but owing to the absorption bands in the spectrum this curve has irregular dips in it; see figure 2. The integration of Planck's equation gives us the area included by the envelope or dotted line, but the determination of the solar constant or integral thermal value gives us the area included by the bolometer curve.

The curve in figure 2 is an observed bolometer curve for sunlight. Dr H. M. Barlow determined for me the ratio between the areas of the envelope (dotted)

* *The Quantum Theory*, p. 129.

curve and of the bolometer curve with an Amsler's planimeter and found it to be 1·135:1. The integration of Planck's equation is easily effected by expanding it in an exponential series.

Then since $$\int x^3 e^{mx} dx = e^{mx}\left(\frac{x^3}{m} - \frac{3x^2}{m^2} + \frac{6x}{m^3} - \frac{6}{m^4}\right),$$

it is easy to prove that

$$\int_0^\infty \frac{8\pi h}{c^3}\left(\frac{\nu^3}{e^{h\nu/kT} - 1}\right) d\nu = \frac{6A}{B^4}\,1{\cdot}082,$$

where $A = 8\pi h/c^3$ and $B = h/kT$.

When the proper numerical values have been put in, the numerical value of the integral is found to be 62·32. But this is the value of the envelope area. Dividing by 1·135 gives us 54·9, or say 55 micro-ergs cm^3 as the mean energy-density.

Hence the value (55 micro-ergs) obtained by the corrected integration of the Planck equation agrees quite closely with that obtained from the Stefan constant, and the four values are as in table 2.

Table 2. Values of mean energy-density of sunlight (micro-ergs cm^3).

From the mean of 10 equidistant ordinates of the Planck curve ...	48
From the solar constant	45
From the Stefan constant	54
From the integration of the Planck equation	55

The last two values are probably the best.

Hence we can say with considerable confidence that the energy per cm^3 of bright sunlight at earth distance is not far from 54 micro-ergs. Bright sunlight gives an illumination of about 13,000 candle-feet at normal incidence on a white surface, and this enables us approximately to determine the radiation-density for other beams of light and also the average number of photons per cm^3, if they actually exist as discrete entities in a beam of light, and we can then calculate the total mass and momentum of these photons and compare it with the mass and momentum of any possible number of electrons which may be set moving along the beam.

e By the relativity theory a stream of photons having total energy e should have a total mass e/c^2 and a total momentum $e\,c$ where $c = 3 \cdot 10^{10}$. Hence for bright sunlight the total photon mass per cm^3 should be $6\ 10^{-26}$ gm. and the total momentum $18/10^{16}$ c.g.s. units or moms.

It is convenient to have a word to express a momentum equal to that of 1 gm. moving with a velocity of 1 centimetre per second. I suggest (with diffidence) the *mom* word *mom* for this unit of momentum. The momentum communicated to a black surface per cm^2 per sec. by bright sunlight is close to 54 micromoms, and the power expended on it is 162×10^4 ergs/sec.

Let us compare these last figures with those of the energy and momentum of an electron current of 1 mA./cm.^{2} flowing *in vacuo* under a voltage-drop of 1 V./cm. This current is equal to 6×10^{15} electrons per second each having a mass of 9×10^{-28} gm. or a total mass of 54×10^{-13} gm. The power expended per cm.^{2} is 10^4 ergs/sec. and hence the velocity of the electrons is given by $v = \frac{5}{8} \times 10^8$ cm./sec. nearly, and the total momentum cm.^{2} is 337 micromoms, nearly. v

§ 3. EXPERIMENTAL TEST

These figures showed that it might possibly be worth while to try whether electrons were hindered or helped in moving against or with a beam of bright sunlight by the momentum of the photons if they exist in such beam.

A preliminary experiment with an arc lamp having shown no result, it was decided to go to the opposite extreme and make use of a very powerful beam of X-rays, the energy of each photon in it being about 10,000 times greater than that of a photon in bright sunlight. The following apparatus was then prepared to test this supposition.

The Director of the General Electric Company's Research Laboratory at Wembley near London was so good as to make for me a special form of Fleming thermionic valve. This valve had a dull-emitter filament which gave quite sensible electron-emission when the filament was not visibly incandescent. It gave this emission when a voltage of 2 volts was placed on the filament terminals, and the filament current was then 0·9 A. The valve had two grid anodes of rectangular shape formed of metal wire fixed on either side. Each grid anode was formed of 18 vertical wires and 27 horizontal wires and had an area of 9 cm.^{2} Each anode was 1 cm. from the filament between them (see figure 3).

Hence when the filament was made active and a positive voltage was put on the anodes an electron current flowed to them. This electron current flowed from the filament in opposite directions to the two grid anodes. If then a beam of radiation was passed transversely across the valve the electrons on one side of the filament moved against the radiation and on the other side with it. A powerful radiation was provided by an X-ray water-cooled hot-cathode tube called a Müller structure tube, which was kindly lent for this purpose by the Chemical Department of University College, London.

The cathode of the X-ray tube was heated with a current of 4·5 A. at 12 V. The potential-difference of cathode and anode was created by 60,000 V. alternating at 50 ~, and the electron current was 21 mA. This tube gave an intense X-ray beam coming out through a circular hole about 1 cm. in diameter, which beam was sent across the thermionic valve transversely to the mesh anodes.

In order that the thermionic valve might be shielded from the electron field of the X-ray tube it was enclosed in an earthed metal case, so arranged that the valve could be rotated quickly to bring either anode nearest to the X-ray tube (see figure 4).

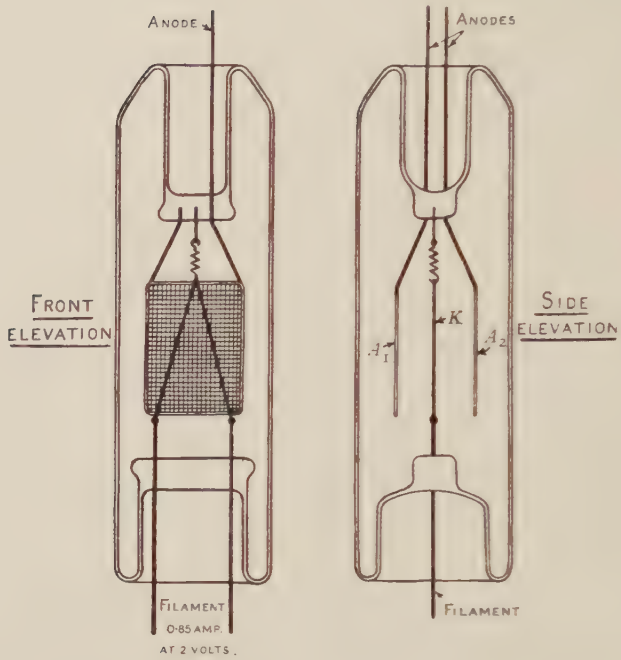

Fig. 3. Special two-anode Fleming thermionic valve with dull-emitter filament.

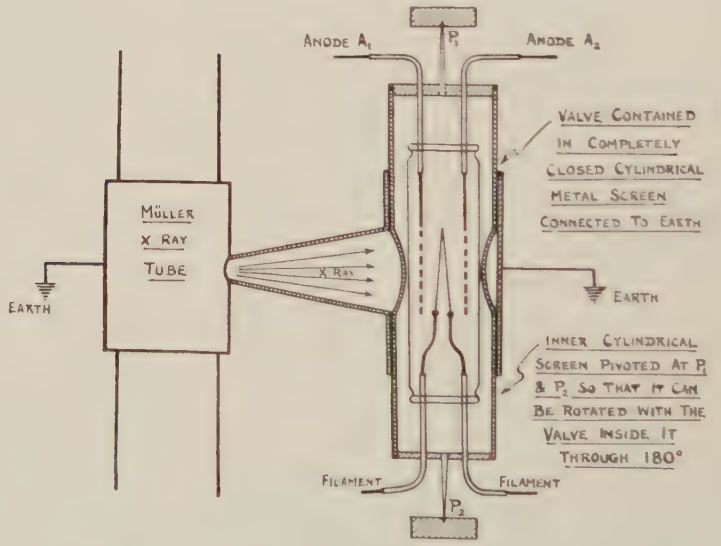
ANODE A_1
P_1
ANODE A_2
VALVE CONTAINED IN COMPLETELY CLOSED CYLINDRICAL METAL SCREEN CONNECTED TO EARTH
MÜLLER X RAY TUBE
EARTH
X RAY
EARTH
INNER CYLINDRICAL SCREEN PIVOTED AT P_1 & P_2 SO THAT IT CAN BE ROTATED WITH THE VALVE INSIDE IT THROUGH 180°
FILAMENT
FILAMENT
P_2

Fig. 4. Two-anode thermionic valve with earthed metal screen round it.

The two grid anodes of the valve were connected to two circuits joined respectively to the two coils of a two-coil Kelvin differential mirror galvanometer of great sensitiveness, and resistances R_1, R_2 were interposed to regulate the currents as shown in figure 5. The anode voltage was supplied by a battery in the common circuit. With an anode voltage of 4 volts the currents through the circuits of the differential galvanometer were each $7{\cdot}4 \times 10^{-6}$ ampere. This then is the electron current to each grid anode of area 9 cm.^{2}, the current-density being 0·82 μA./cm.^{2}

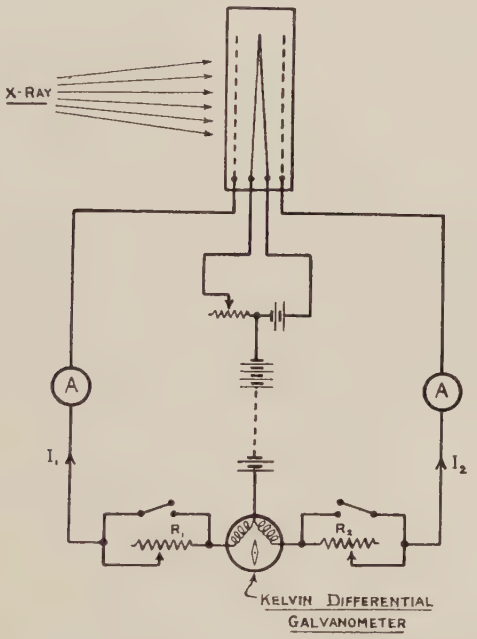

Fig. 5. Arrangement of circuits with two-anode valve for testing the effect of an X-ray beam upon a stream of electrons.

The experiment then consisted in noting whether the incidence of the X-ray beam produced any steady variation from equality in the two electron streams to the two anodes of the valve. No permanent change was however observed in these two electron currents under the continuous action of the X-ray beam. The galvanometer could have detected any change in each electron current which was greater than $3{\cdot}5 \times 10^{-9}$ A.; that is, it could have indicated a change of 1 part in 2000 or 0·05 per cent of the anode electron-currents to the grids. But no change as great as this was found. Hence to that extent the X-ray beam does not alter the electron stream. The same negative result was found when the thermionic current in the valve was given other and greater values.

We can make a rough estimate of the relative energy and total momentum of the electron stream and the X-ray beam as follows. We cannot estimate the energy-density of the X-ray beam by any calorimetric measurements as in the case of sunlight, but we may assume as an approximation that every electron which comes

out of the hot cathode of the X-ray tube and strikes the anticathode generates one photon or quantum and that this is driven against the grid anodes of the valve.

Now the cathode current of the X-ray tube was 21 mA., equal then to $126 \cdot 10^{15}$ photons per second striking the grid anode of area 9 cm.², or to $14 \cdot 10^{15}$ photons per sec. per cm.² The frequency of this X-ray is roughly 10,000 times that of visible light, and hence the energy of each X-ray photon would be about $10{,}000 \cdot 36 \cdot 10^{-13}$ erg by table 1, to 36×10^{-9} erg. The total energy of all the photons would then be 504×10^{6} ergs per cm.² of anode. The total momentum is obtained by dividing this last number by 3×10^{10} which gives $168 \cdot 10^{-4}$ mom or 16,800 micromoms per cm.²

When an anode voltage of 4 volts was put on the thermionic valve the current to each grid anode was 7·4 μA., which is equivalent to $44{\cdot}4 \cdot 10^{12}$ electrons per sec., or to 5×10^{12} electrons per sec. per cm.² of grid surface. The mass of each electron, neglecting the small relativity increase, is $9 \cdot 10^{-28}$ gm. and hence the total electron mass is 45×10^{-16} gm./cm.² The power given to each anode is then nearly 300 ergs/sec. or 33·3 ergs/sec. per cm.² of grid surface.

Hence if m is the total electron mass and v the r.m.s. electron-velocity we have $\frac{1}{2}mv^2 = 33{\cdot}3$ ergs or $v = 1{\cdot}25 \times 10^{8}$ cm. sec. The electron-momentum expended per second against each cm.² of grid surface is $56 \cdot 10^{-4}$ mom or 0·56 micromom.

Accordingly we can compare the energy and momentum of the above electron stream and photon stream per cm.² of grid as in table 3.

Table 3.

Imparted per second	By electron stream	By X-ray beam
Energy (ergs per cm.² of grid)	33·3	504×10^{6}
Momentum (micromoms per cm.² of grid) ...	0·56	16,800

Hence even making the widest allowance for errors or rough approximation we see that the energy and momentum of the photons in the X-ray beam must have been enormously greater than that of the electron stream flowing to each grid anode; yet they did not affect that current even to the extent of 0·05 per cent.

On the other hand it may not be altogether a question of total momentum but of the chances of a collision between an electron and a photon, which may depend on their relative size and number. In the present case we estimated that $5 \cdot 10^{12}$ electrons struck each grid anode per sec. per cm.² and that their velocity was 125×10^{8} cm./sec. Hence there must be 4×10^{4} electrons per cm.³ Taking the square of the cube root of this number, viz. 1169, shows us that in this case there are about 12 electrons per mm.² of cross-section of the current.

Again we estimated that $14 \cdot 10^{15}$ photons moving at $3 \cdot 10^{10}$ cm. sec. would strike every cm.² of grid area. Hence 466,000 photons should exist in every cm.³ This gives about 6000 per cm.² of section or 60 photons per mm.² The chance of any considerable number of photons or X-ray quanta colliding with an electron

and reducing or decreasing its momentum must depend on the actual and relative size of electrons and quanta, and this is indeterminate.

On certain assumptions we may consider that the diameter of an electron is 10^{-13} cm. and its apparent area 10^{-26} cm^2, but we know nothing about the possible size of light quanta. The absence of any effect upon the electron speed produced by the X-ray beam may be due to the very small probability of a photon hitting an electron, and not to the entire absence of photons as mass particles. The fact that when radiation energy enters or leaves an atom it does so in certain quanta of defined amount, $h\nu$, does not necessarily imply that these quanta travel through space as defined and discrete particles of energy, maintaining so to speak their identity during travel. If for instance water were being put into a canal in whole bucketsful at a time in one place and drawn out in whole bucketsful at another place the water would not travel along the general mass of the canal water as bucketsful.

Again, even if the quanta or photons have any objective existence in space the probability of a collision with electrons may be a question of dimensions. Thus if we were shooting with a shot-gun at a covey of birds covering a certain area of the sky the chance of bringing down a bird would be greater the larger the bird and the larger the shot.

In the well-known Compton effect, A. H. Compton found that light quanta or photons could apparently rebound from electrons tethered in atoms and that the ordinary dynamical laws of impact were obeyed*. In the case of the experiment above described with the thermionic valve, the electrons were free and distributed widely over a large cross-section area. Hence the two cases are not identical and from the fact of the Compton effect we cannot infer that there are necessarily free photons in an X-ray beam or in a beam of light†.

§ 4. CONCLUSION

The conclusion which seems legitimate from the negative results of the above described experiments is either that the light quanta or photons do not exist as defined mass particles during transmission of light energy, or else that the total apparent area covered by the photons in the cross-section of a beam of radiation must be relatively very small compared with that cross-section, and the same also for a current of electrons flowing with or against that beam. Or to put it in another way, the probability of a photon and an electron occupying the same area at the same time is very small, since the ideas now current in connexion with the wave-mechanics theory of matter forbid us to think of the electron or of the photon as having any definite size.

* A. H. Compton, *Phys. Rev.* **21**, 207, 483 (1923).

† W. M. Hicks, "The Nucleus as Radiator." *Phil. Mag.* **8** (1929).

§ 5. ACKNOWLEDGMENT

Lastly I must record my thanks to Professor W. C. Clinton, B.Sc., for affording me facilities for these experiments in the Electrical Engineering Laboratories of University College, London, and also to Professor E. G. Coker, F.R.S., for kindly allowing facilities for conducting them in a room in his laboratory and particularly to Dr H. M. Barlow for carrying out all my suggestions for these experiments with great skill and care.

DISCUSSION

The PRESIDENT read the following extract from the minute-book:

"A meeting of the Society was held in the Physical Laboratory, South Kensington Museum at 3 p.m. on Saturday, March 21, 1874.—Dr Gladstone in the Chair. There were about 35 members present.

"The Chairman gave a brief description of the objects and organization of the Society and noticed the very favourable circumstances under which this Society originated as compared with those attending the origin of its parent the Royal Society. He announced that ninety-nine gentlemen had already expressed their desire to join the Society as original members.

"J. A. Fleming, B.Sc., read a paper on the new contact theory of the galvanic cell. Professor F. Guthrie exhibited experiments illustrating the distribution of a galvanic current on entering and leaving a conducting medium."

Dr W. N. BOND. The author mentions the difficulty of measuring the amount of energy conveyed by the X-ray beam; and he makes a rough estimate by assuming that each electron which strikes the anti-cathode of the X-ray tube generates one photon or quantum, which then passes through the thermionic valve. Calorimetric measurements of the energy conveyed by an X-ray beam have, however, been made by several physicists. In calorimetric experiments that Prof. J. A. Crowther and I carried out*, the conditions seem to have been comparable with those described in the present paper. We used a Shearer tube with molybdenum anti-cathode, working on a transformer. When the peak value of the applied voltage was 55,000, the current about 3 m.A., and the mean wave-length 0·6 A., energy was conveyed by an X-ray beam of solid angle 0·06 at the rate of a calorie in two hours. This would imply that the rate of supply of energy by the X-ray beam was only about 1/10,000 of that estimated (table 3). If the present experiments were used to place an upper limit to the size of the photon, this correction would have to be applied.

Dr L. SIMONS. In connexion with this work it is appropriate to say that Hughes and Jauncey† endeavoured to detect collisions between photons by directing two focussed beams of light towards one another. Observations for scattering effects were made at the point of impact of the two beams, with negative results. The

* *Phil. Mag.* **6**, 401 (1928).

† *Phys. Rev.* **36**, 773 (1930).

conclusion was reached that the cross-section area of a photon was not greater than $10^{-10}\,\lambda^2$.

Dr D. Owen. This is certainly a highly interesting experiment on a subject of importance in regard to present-day theories of photons and the electron. It has a special interest also in that the electronic valve is used by its distinguished inventor as an instrument of research into the recondite relations between electricity and light. From the negative results obtained, Sir Ambrose concludes that either light quanta do not exist, or that the chances of collision of a light quantum or photon with an electron, when beams of these traverse one another, must be very small. The former conclusion would seem to be already disposed of by the fact of the Compton effect, the existence of which has been amply demonstrated not only as regards the change of frequency of the scattered radiation, but also (from the work of C. T. R. Wilson and others on cloud tracks) as regards the velocity of the recoil electrons. It therefore seems that experiments of the type described in the paper should be regarded as means of determining, or at least of assigning a lower limit to, the chances of collision of a photon and an electron. From the results in table 3 the ratio of the momentum per cm.^{3} of photons in the X-ray beam and of electrons between grid and anode of the thermionic valve is 16,800/0·56, that is, 30,000. The least detectable change of momentum of the electron beam is found to be 1/2000. The product of these factors is 60×10^6. This figure, however, appears to be a considerable over-estimate in two respects. First, the assumption that every electron impinging on the anti-cathode of the X-ray tube generates a photon of wave-length 0·5 Å. gives an efficiency of conversion of electrical energy into X-ray energy which is obviously far too great, working out indeed to be practically unity, whereas a figure of 1/1000 is probably nearer the mark. Next, the calculation assumes that all the photons liberated at the anti-cathode of the X-ray tube find their way to the anode of the valve, whereas it is only the fraction within the solid angle subtended by the anodes at the anti-cathode that are operative, and from the dimensions of the apparatus this fraction appears to be about 1/150. Thus the figure of 60×10^6 is reduced to about 400. If it is now assumed that every encounter of photon with electron is head-on, the negative result of the experiments would be accounted for if fewer than one photon out of 200 makes such a complete collision in its passage through the electrons within the valve. Such a conclusion is not in the least surprising when it is remembered how small is the absorption coefficient for X-rays of even a gas at atmospheric pressure, and that whereas here some 10^{19} gas molecules are present per cm.^{3}, in the grid-to-anode space of the valve the number of electrons per cm.^{3} is only 40,000.

The difficulties attending the theoretical aspect of experiments of this nature are illustrated by a quotation from Sir James Jeans's *Report on Radiation and the Quantum Theory*: "A free electron cannot accept a quantum of radiation under any circumstances whatever.... The simplest structure which can absorb a quantum of energy is a complete atom." (2nd ed., p. 83.) So that, after all, the experiment was foredoomed to be hopelessly negative!

Author's reply. A negative result in an experiment is never so interesting as a positive result; nevertheless, the negative result may not be without value if the conditions of the experiment or assumptions made in deductions from it are carefully stated; and this I endeavoured to do in the present paper.

I am glad to be corrected by Dr W. N. Bond on the point of the calorimetric measurement of X-ray energy, and I regret that I had overlooked the paper by Prof. J. A. Crowther and himself. I pointed out, however, that even if the widest allowance is made and if only 1 photon is assumed per 1000 incident electrons in the X-ray tube, the excess of photonic momentum in the thermionic valve is very great. I quite admit that my means of determining any change in the electron current of the thermionic valve by the X-rays was not extremely refined; yet, even in face of the weighty opinion of Dr Owen and the deductions from the Compton effect, the fact remains that no one has given any sufficient proof that a photonic theory of light will explain interference and diffraction effects or the manner in which waves without energy can guide photons with energy so as to produce these effects.

If time had permitted I should have endeavoured to show from certain facts in radio-telegraphy that a pure wave theory may yet explain how it is that only a very few atoms of a gas are ionized by an X-ray beam, a fact which has always been one of the supports of a photon theory. That, however, is a long story.

THE SPHERICAL SHELL METHOD OF DETERMINING THE THERMAL CONDUCTIVITY OF A THERMAL INSULATOR

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Received October 2, 1931. *Revised January* 13, 1932. *Read and discussed February* 19, 1932

ABSTRACT. The spherical shell method of determining thermal conductivity has been applied to a thermal insulator in a system of comparatively small dimensions, the outer diameter of each of the shells employed being roughly 10 cm. Sulphur was selected as the material under test, and the spherical shells were cast in a brass mould. The supply of heat to the centre of the system was maintained electrically, a power-supply of 2 watts producing a temperature-drop of approximately 10° C. across the specimen. The range of temperature covered by the experiments was from 5° C. to 85° C. The results obtained are compared with those derived for sulphur by other observers.

§ 1. INTRODUCTION

THE method of determining the thermal conductivity of a substance by using the material in the form of a spherical shell and observing the steady difference between the temperatures of the surfaces due to a constant flow of heat from the centre has been employed by a number of investigators. Using this method for a good conductor Laws, Bishop and McJunkin [1] experimented on a cast-iron shell having an outer diameter of 6 in. and a thickness of 1·4 in., while Bishop [2] afterwards applied the method to the determination of the thermal conductivity of lead, using a specimen of roughly similar dimensions. In the case of a number of thermal insulators the spherical shape was adopted by Nusselt [3], who filled with the material under test the space between two concentric metal spheres, the inner one being of copper and the outer of zinc. The diameters of these spheres were 15 cm. and 65 cm. respectively. The temperature at a number of points within the specimen being determined by means of thermocouples, care was necessary to ensure that the leads of each couple lay in the isothermal surface for some centimetres from the junction. Neglect of this precaution was shown to give rise to large errors. Among the substances tested were such loose materials as sawdust, cotton, charcoal and asbestos.

The experiments outlined below were conducted in an attempt to determine the thermal conductivity of a poor conductor by the use of a spherical shell of relatively small dimensions, the inner and outer diameters being roughly 5 cm. and 10 cm. respectively.

Over other methods which involve only measurements made under the conditions of thermal equilibrium, with the consequence that the density and specific

heat of the specimen do not enter into the calculation, the spherical shell method possesses advantages from the theoretical point of view. The uniform distribution of the lines of heat-flow leads to an easily determined shape-factor, while there is the absence of a correction such as that which arises from the heat-loss at the edges of a flat plate. The attempt to realize these advantages as far as possible in practice in the case of a small shell of badly conducting material necessitates particular attention to some experimental details. In the first place, the passage of the necessary leads through the shell to supply heat to the inner surface and to register its temperature produces a heat-loss which is the more important the smaller the conductivity of the specimen. Further, the smaller the dimensions of the shell the more important does accurate concentricity of the inner and outer surfaces become.

In the present investigation sulphur was chosen as the substance under test. Most thermal insulators being composite materials, sulphur has the advantage that as an element it is not susceptible to variations in the values of its physical constants from specimen to specimen. Its melting point (115° C.) was conveniently low for making castings, while the solid state was retained well above the maximum temperature, 80° C., at which the thermostat controlling the temperatures of the observations would operate satisfactorily. From this point of view sulphur was preferable to waxes, to which the method is equally applicable.

§ 2. OUTLINE OF THE METHOD

Each shell of sulphur was cast between two concentric spherical surfaces provided by the outer surface of a sphere of brass *A*, figure 1, and the inner surface of a spherical shell *B*, also of brass. A steady source of heat was supplied by the passage of an electric current through a 6-volt lamp enclosed within the inner sphere, the interspace between the lamp and this sphere being filled with mercury. The vertical aperture in the casting which permitted the insertion of the source of heat was plugged with sulphur. The system was immersed in water to within a few millimetres of the top of the neck of the outer brass casing, the temperature of the water being maintained constant by an electrically controlled thermostatic device. For a given power-supply at the centre of the system the corresponding steady difference between the temperatures of the inner and outer sulphur surfaces was measured by means of thermocouples. One of these was placed in a glass tube suspended in the water bath, and the other in an aperture let into the inner brass sphere. Under the conditions of experiment the falls of temperature across the metal shells were small and calculable. The inner brass sphere was made thick (1·5 cm.) in order that it might render uniform the temperature of the inner surface of the specimen. If W_1 be the power-supply, θ_1 the difference of temperature attained in the steady state, and K_1 and K the apparent and true thermal conductivities respectively of the material under test, then

W_1, θ_1
K_1, K

$$W_1/\mathcal{J} = K_1 S\theta_1 = KS\theta_1 + H \qquad \ldots\ldots(1),$$

S, H

where S is the shape-factor of the shell and H represents the heat lost by conduction along the inner thermocouple wires and the power leads. For this loss a correction

was applied. The orders of power-supply and current used were 2 W. and 0·4 A. respectively, the temperature-intervals across the specimen varying from 7° C. to 17° C.

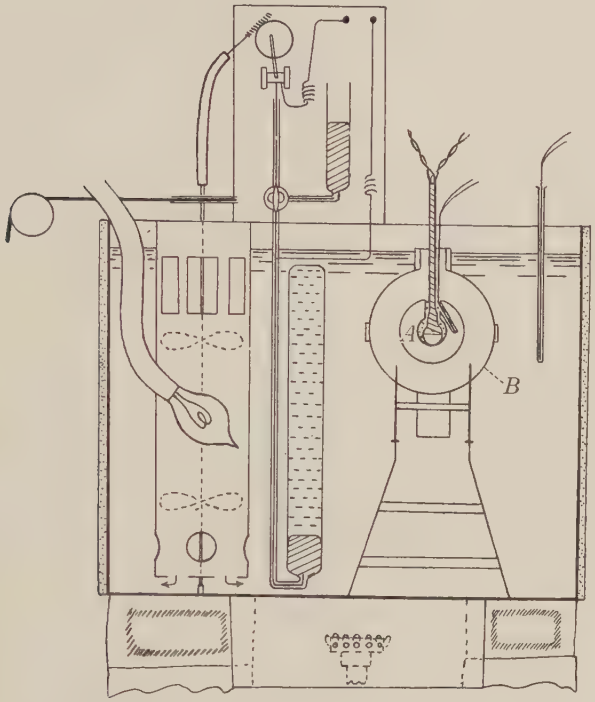

Fig. 1. Schematic view of the apparatus.

§ 3. THE CASTING OF A SHELL

The mould. The mould system was entirely of brass. The outer casing consisted of two hemispherical shells *A* and *B*, figure 2, which screwed together horizontally. The inner surfaces were accurately worked to the same radius and when the two sections were in position the lower rim *r* of the upper shell terminated in the horizontal diametral plane of the inside spherical surface. The lower shell carried a stout cylindrical boss provided with flats to facilitate gripping in a vice. Into the neck *C* at the top of the upper hemisphere screwed a tube *D*, its axis coinciding with the vertical diameter of the inner spherical surface.

The inner sphere also was made in two parts *G* and *H* which screwed together horizontally, in this case the outer surface of each section being accurately worked to the same radius. The rim *s* at the base of the upper portion *G* terminated in the horizontal diametral plane of the outer spherical surface formed when the two parts were screwed together. Into the top of the upper section *G* screwed a tube *K* coaxially with the vertical radius. When the mould system was centred as shown in the figure the inner tube overlapped the outer by some 3 cm., the protruding portion being a hexagonal head of slightly smaller diameter than the main cylindrical

section. The head E of the outer tube D was hexagonal also. Each of the upper hemispheres screwed to a shoulder on the corresponding tube, thereby ensuring that insertion of the tube was always made to the same depth. The inner system could be suspended within the outer by means of six bolts such as b, b screwed up to grip the inner tube, the bolts being in two horizontal groups 120° apart in each. Two well-fitting collars l, l were made to slide over the ends of the inner tube into the annular space between the tubes, a projecting head on each collar facilitating its withdrawal when necessary.

Dimensional data of the mould are as follows. The effective spherical surfaces had radii of 2·8 cm. and 5 cm. respectively, the corresponding shells being 1·5 cm.

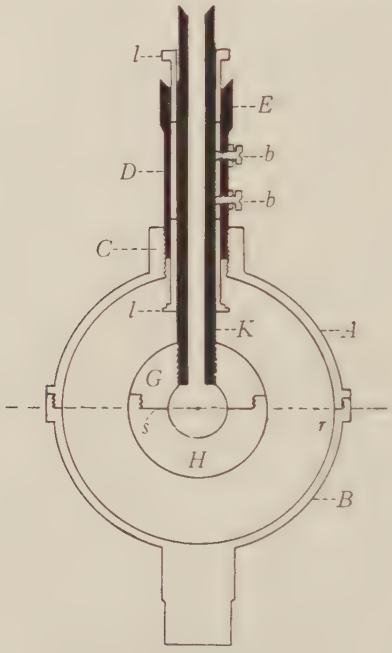

Fig. 2. The mould system.

and 0·3 cm. in thickness. The length and diameter of the inner tube were 17 cm. and 1·9 cm. respectively. The outer diameter of tube D was 2·6 cm. and the annulus between the tubes 0·22 cm. in depth.

Prior to the setting up and adjustment of the mould the walls of this annulus were treated with castor oil to impede the adhesion of sulphur to them. The oil also facilitated the extraction of the collars when necessary. The operation of rendering concentric the surfaces between which the casting was to be made was carried out in the following way. The mould system as shown in figure 2, but with the lower hemispheres B and H removed, was inverted and clamped by the head E on the outer tube, the bolts lightly gripping the inner tube. The collars being in position, motion of the centre of the inner spherical surface was confined to the vertical centre-line common to the two spherical surfaces. Thus only in the vertical

direction was adjustment of the inner surface required. The elevation of the inner tube was adjusted until a straight edge placed across the rim r of the outer shell just touched the rim s of the inner sphere. By tightening the bolts the inner tube was then locked in position. The inner hemisphere was unscrewed to permit the withdrawal of the collar and was then replaced. The remaining hemispheres were screwed into position to complete the spherical surfaces. The system was removed from the vice and the upper collar extracted. The adjustment of the mould was now complete.

The tube system served a dual purpose. It provided means whereby the components of the mould could be centred, and supplied, in the space between the tubes, a reservoir from which liquid sulphur could be drawn as solidification proceeded within the shell.

The casting process. In making a casting it was necessary to ensure that the sulphur cooled slowly and solidified from the bottom upwards. An electric heater was used to control the temperature of the mould, the entire outer surface of which was insulated by a layer of asbestos paper pasted on in the form of strips. The heater consisted of bare nichrome wire wound directly on to the asbestos coating. The frame necessary to keep the heating-wire in position on the spherical portions of the mould surface consisted of four narrow wire helices tied on by means of thread so as to lie vertically on lines of longitude 90° apart. Each helix was of cotton-covered copper wire further insulated, before being mounted, by repeated dipping in shellac varnish. The spacing of consecutive turns on each helix just permitted the insertion of the heating-wire.

The inner mould, receiving heat chiefly by conduction through the bolts at the top, was always coldest at the bottom. To obtain the same condition in the outer mould the heater was wound horizontally to give a gradually increasing concentration of heat-supply from the bottom upwards. The windings on the lower hemisphere were separated by three turns of the helices, while from the equator upwards the spacing passed from two turns to one, the outer tube being covered by practically contiguous turns of heater wire. Finally, a few turns were wound round the projecting portion of the inner tube. No windings were placed round the boss at the base of the mould. The whole system was heavily lagged. The length of heater wire employed was about 15 metres, the total resistance being roughly 20 ohms.

During the process of casting the temperature of the system was indicated approximately by a thermometer resting inside the inner sphere. A current of 1·2 A. was sufficient to keep the temperature steady at about 170° C. The liquid sulphur, obtained from sulphur flowers, was poured while at a temperature of 160° C. into the top of the mould down the annulus between the two tubes, until there were signs of overflow. The adhesion of air bubbles to the brass was impeded by polishing the inner surfaces of the mould before assembly and by tapping the mould when it contained the liquid. After filling, the heating current was reduced by 0·05-ampère stages, being maintained constant at each value for 10 to 12 minutes. Liquid sulphur was continually added to keep the space between the

tubes full. When the current reached the value 0·8 A. solidification was complete. A current of 0·5 A. was passed for half an hour, the system then being allowed to cool in the lagging.

After removal of the heater and asbestos insulation from the mould the bolts and tubes were extracted, the latter by turning at the hexagonal heads. In spite of the initial smearing of the appropriate surfaces with castor oil it was found necessary, in the case of most of the castings, to warm the tubes before they could be turned. The sulphur broke off at the base of the outer tube, which point (see figure 2) was well up in the neck of the outer casing. Completion of the casting to the top of this neck was effected by pouring liquid sulphur into the neck with the inner tube in position.

A very slow rate of cooling during the casting process was essential, not only to secure a uniform specimen but also, since sulphur contracts on freezing, to guard against possible recession from the mould surface. That satisfactory contact was established between this surface and the casting is indicated by the great tenacity with which sulphur was found to adhere to brass even when allowed to solidify quite rapidly.

§ 4. FURTHER EXPERIMENTAL DETAILS

The location of the inner thermocouple. This is shown diagrammatically in figure 3. In a preliminary series of experiments the attempt was made to register the temperature of the inner surface of the sulphur shell by placing the inner thermocouple in a narrow channel *c* cut round the periphery of a vertical diametral section of the inner sphere, the channel being covered in by brass strip. Prevention of leakage of the sulphur past the shoulder at the top of the screw thread on the inner tube proved, however, to be troublesome. The couple junction was therefore placed on the horizontal diametral plane of the inner brass sphere, approximately mid-way between its inner and outer surfaces. To effect this a cylindrical channel *d* was drilled through the upper section of the sphere and inclined at roughly 55° to the horizontal. This channel, 3 mm. wide, was duplicated on the opposite side of the upper section of the sphere in the same vertical diametral plane. Leakage of sulphur into these channels was prevented by treating the thread of the inner tube with a mixture of graphite and seccotine prior to the erection of the mould. As indicated in the figure these thermocouple orifices lay in a plane at right angles to that containing the outer channels originally used. This method of locating the couple had the advantage that the insertion and extraction of the wires were facilitated, owing to the absence of a pronounced bend such as was entailed in the first case.

The lamp and plug system. The 3-watt screw-on-type lamp employed to supply heat to the system was of a length 2·8 cm., so as to be enclosed within the inner brass sphere when standing vertically bulb downwards. The current leads, consisting of flex wire equivalent in section to no. 22 s.w.g., were supported by a thin ebonite rod some 10 cm. long. The metal thread covering the base of the lamp was insulated by a binding of tape and a coating of collodion. The tape binding was continued

round the leads and rod, near the top of which the potential leads were joined to the current wires. Separate potential leads to the lamp itself were not used owing to the additional heat-loss which would thereby be entailed.

The procedure adopted in casting the sulphur plug surrounding the lamp leads was the following. Sufficient mercury was poured into the orifice of the shell to raise the level just above that of the entrances to the outer channel *c*, the uppermost portions of which, being unoccupied by sulphur, were thus filled with the liquid. The system having been brought to a temperature in the vicinity of 0° C. by being left in an ice bath for four hours, mercury was extracted until the surface was just

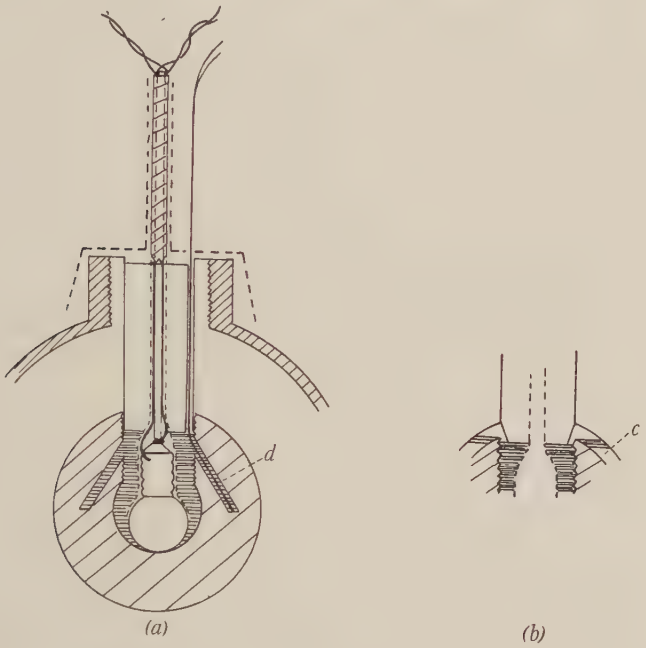

Fig. 3. The lamp and plug system. (*a*) and (*b*) are vertical central sections at right angles to each other.

below the entrances to the outer channels when the lamp was inserted into the orifice and held with the tip of the bulb touching the underside of the inner brass sphere. The lamp-lead system being kept at this depth by a frame which clamped on to the neck of the outer casing, the plug was cast by pouring liquid sulphur down the orifice, which acted as the mould. Contact with the sulphur wall of the orifice and leakage into the outer channels of the inner brass sphere were prevented by covering the surface of the orifice with a thin layer of paper which terminated below the level of the mercury. The paper was treated with glycerin to make it slightly adhesive, and remained attached to the sulphur plug on removal of the lamp system. The base of the plug was cut away a little at the points opposite the outer channels to give free access of mercury to them. A narrow vertical groove was cut along the plug to accommodate the thermocouple leads. Before the plug was

finally inserted for the conductivity measurements, the walls of the orifice were treated with glycerin to give good thermal contact. By casting the plug in this way with the system at 0° it was ensured that the mercury remained in contact with the base of the plug at all temperatures, while the expansion of the mercury at the higher temperatures was taken up within the inner brass sphere.

The sphere system was mounted on a tripod in a 20-gallon copper tank, figure 1, provided with an electro-thermal regulator similar in type to that described by H. T. Barnes [4]. In this method of temperature-control the expansion of a quantity of toluol, contained in a bulb immersed in the water filling the tank, actuates a relay through the medium of a thread of mercury in a glass tube leading from the bulb. The circulation of the water was in such a direction as to leave the surface undisturbed. At the higher temperatures the water was covered with a layer of oil to impede evaporation. The bath being lagged with asbestos, sufficient energy to control the temperature was available from the two 20-watt lamps used as heaters in the water, provided the temperature was not more than about 6° C. above that of the laboratory. For higher temperatures a small spray gas flame was maintained underneath the thermostat, which was raised on a brick support for this purpose. The electric regulator then acted as a fine adjustment. For temperatures close to that of the surrounding air it was necessary in conjunction with the use of the regulator to pass a stream of cold water through a coil of tubing immersed in the bath. To obtain an ice bath the regulator was removed and ice water was kept in circulation.

The thermocouples used consisted of fine constantan and copper elements (36 s.w.g.), the wires passing into the sphere being further insulated and strengthened by repeated dipping in a mixture of collodion, acetone and castor oil. The length of this couple lying within the orifice cut to receive it in the inner sphere was approximately 2 cm. That this immersion was adequate to avoid appreciable error due to conduction along the leads was tested experimentally on a number of occasions. On raising the couple junction 3 mm. the alteration in the differential thermo-electric e.m.f. was less than could be detected with certainty, being lower than 1 in 1000.

In determining the temperature-interval use was made of the relation

$$E_{t_1} - e \cdot \frac{E_{100}}{s_{100}} + E_{t_2} \frac{b_{100}}{s_{100}} = e\,(1+\lambda) + E_{t_2}\,(1+\beta) \qquad \text{.....(2),}$$

t_1, t_2 in which t_1, t_2 are the temperatures of the hot and cold junctions respectively, the
$_{100}$, b_{100}, E e.m.f.'s of which at 100° C. are s_{100} and b_{100}; while E denotes an e.m.f. on the standard
λ curve given by L. H. Adams [5]. The correction λ to the observed differential e.m.f.
e, β e was approximately 0·003, the value of β being generally negligible. The bath temperature was observed by means of standardized mercury thermometers. Owing to the slow change of slope of the standard e.m.f. curve, the correct evaluation of $(t_1 - t_2)$ did not require very great precision in the estimation of the thermostat temperature.

The shape-factor of the casting, $4\pi Rr\,(R-r)$, required for its determination

the measurement of the radius of (*a*) the inner surface of the outer brass shell and (*b*) the outer surface of the inner brass sphere. Measurement of the former was effected by screwing together the two sections of the outer shell and weighing it before and after it had been filled with distilled water. In order to ensure that for each determination the sphere was exactly filled with the liquid, a brass stopper provided with a fine central orifice was made to screw down into the neck of the upper hemisphere. When the stopper was in position its lower surface, which was shaped to the appropriate radius, completed the spherical surface under test. The radius of the outer surface of the inner brass sphere was determined from a system of calliper measurements. By marking the sections of the shell and the sphere it was secured that in assembling the mould the sections were screwed into the identical relative positions occupied during the determination of the radii.

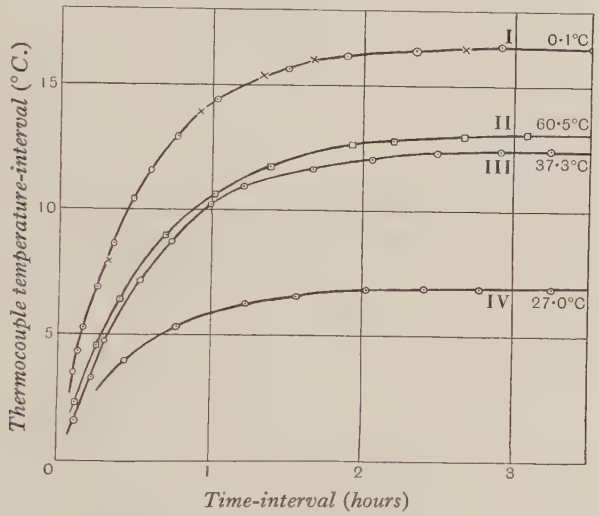

Fig. 4. Mode of attaining thermal equilibrium.

The time taken to attain thermal equilibrium. The manner in which after the heating current was started the temperature of the inner surface of the specimen rose to the value corresponding to thermal equilibrium was determined by observing the time at which the e.m.f. of the differential couple system attained in turn each of a series of suitably spaced values. A selection of the curves so obtained for various power-supplies is given in figure 4, the temperature alongside each curve denoting the thermostat temperature in each case. The extent to which the variation of temperature was of exponential form is indicated in the case of curve I, the ordinates denoted by crosses being calculated from the expression $\theta = 16{\cdot}54\,(T - e^{-0{\cdot}0335t})$ in which the time t is measured in minutes. Curve IV is a plot of observations taken with a double-lead system such as is described later.

During an interval of from 3·0 to 3·5 hours from the commencement the temperature rose by only about two parts in a thousand. The thermal-conductivity

values were determined from the temperature-difference obtaining after approximately four hours had elapsed from the starting of the heater current. During this interval the power-supply was checked from time to time on a four-dial potentiometer of Kelvin-Varley type and was found in general to be constant to one part in a thousand during the last hour. The value during the latter period was taken for the conductivity measurement in each case.

The effective temperature of experiment. Since in the steady state the temperature-gradient along any radial line of the shell was not constant but varied as $1/x^2$ where x is the radius of any elementary shell of thickness dx, it was necessary to define the temperature (called for convenience the effective temperature) to which the deduced conductivity corresponded. The heat-flow Q per second across any elementary shell having a temperature θ is given by

$$Q = -4\pi x^2 K \cdot \partial\theta/\partial x,$$

in which K is a function of the temperature. If with sufficient accuracy the variation with temperature of the conductivity of the specimen may be taken as linear over the range obtaining in any one experiment, and if for the purpose of evaluation the temperatures of the inner and outer surfaces of the shell be taken as θ_1 and zero respectively, then by integration

$$\frac{Q}{4\pi x} = \int K_0 (1 + \alpha\theta)\, d\theta + B,$$

in which K_0 is the thermal conductivity at the temperature of the outer surface.

Hence $$Q/4\pi x - Q/4\pi R = K_0 (\theta + \tfrac{1}{2}\alpha\theta^2),$$

i.e. $$Q/4\pi r - Q/4\pi R = K_0\theta_1 (1 + \tfrac{1}{2}\alpha\theta_1).$$

Thus $$Q/S = K_m\theta_1 \qquad \text{.....(3),}$$

where K_m is the thermal conductivity of the material at the temperature midway between those of the surfaces of the shell. Since the results obtained throughout the range of temperature explored (5° C. to 85° C.) indicated a linear variation with temperature of the conductivity of the specimen, the effective or mean temperature corresponding to each experiment was given by the addition of the thermostat temperature to half the drop across the shell.

A specimen calculation of the apparent thermal conductivity of the casting is as follows.

Data relating to shape-factor: outer radius $R = 5{\cdot}100$ cm.; inner radius $r = 2{\cdot}757$ cm.; $S = 75{\cdot}4$ cm.; bath temperature $= 40{\cdot}7$° C.; e.m.f. of differential couple system $= 778$ μV.; corresponding temperature-interval $\theta_1 = 17{\cdot}99$ C.; mean temperature of experiment $= 55{\cdot}7$° C.

Power-supply: current $= 0{\cdot}4790$ A.; e.m.f. $= 7{\cdot}006$ V.; power $= 3{\cdot}356$ W.

Apparent thermal conductivity $= W_1/\mathcal{J}S\theta_1 = 0{\cdot}00059_2$ cal./cm.-sec.-degrees.

Corrections to be applied to the results. Correction for heat-loss. The question of heat-loss was simplified by the absence of a stirring device at the centre of the

system, since uncertain corrections for stirring and for conduction along the stirrer shaft were avoided. Neglecting any possible loss from the surface of the sulphur at the top of the neck of the casing, which loss would in any case be very small, there remained the heat lost by conduction along the current leads and the inner thermocouple elements. The problem of making any theoretical assessment of the value of this loss was complicated by the fact that while the lower portions of the couple wires were at the temperature of the inner brass sphere, the lower parts of the current leads, being attached to the lamp itself and insulated from the mercury, were at a temperature considerably higher by an unknown amount than that of the inner sphere. This made the ratio of the loss along the current wires to that along the couple elements greater to an uncertain extent than the value corresponding to the ratio of the cross-sections. The total loss was eliminated in the following way. An additional determination of the apparent conductivity was made in which the current leads and couple wires were duplicated in exactly the same positions, the other conditions (such as power-supply, mean temperature of experiment, and temperature-drop across the shell) being reproduced as nearly as possible. Although the electric current-densities in the power leads were unequal in the two cases, the dissipation of energy (of the order of 0·001 W.) in these leads was, judging by the results obtained, insufficient to materially affect the conduction of heat along them. The heat-loss obtaining in the primary experiment was thus approximately doubled.

For a primary determination with single leads the relation giving the heat flow per second is given by

$$Q_1 = W_1/\mathcal{J} = K_1 S\theta_1 = KS\theta_1 + H \qquad \text{.....(1),}$$

where H is the heat-loss along the wires and K_1 and K the apparent and corrected conductivities respectively of the material. *H*

Similarly for an experiment with double leads and approximately the same temperature-interval θ_2

$$Q_2 = W_2/\mathcal{J} = K_2 S\theta_2 = KS\theta_2 + 2H \qquad \text{.....(4).}$$

Hence it follows that

$$K = K_1 - (K_2 - K_1)\,\theta_2/(2\theta_1 - \theta_2) \qquad \text{.....(5),}$$

while the fractional heat-losses are given in the respective cases by the expressions

$$(K_1 - K)/K_1 \quad \text{and} \quad (K_2 - K)/K_2 \qquad \text{.....(6), (7).}$$

The heat-loss could thus be corrected for, in the absence of any arbitrary assumption as to its precise nature or as to the relative importance of the losses along the current leads and thermocouple elements. In the case of the secondary experiments with double leads a lamp exactly similar to that used in the primary observations was employed, and a plug was cast round the duplicated lead system as before. An additional copper thermocouple element was laid alongside the inner thermocouple wires and immersed to the same depth. It was unnecessary to duplicate the constantan element since the heat-loss along it was negligible, being only about one-twentieth of that due to the copper element.

Drop of temperature across the mould components. The difference between the temperatures of the thermocouple junctions was very slightly greater than the temperature-drop across the specimen. By calculation the fall of temperature across the 7 mm. of brass intervening between the inner thermojunction and the inner surface of the sulphur shell was 0·02° C. for a power-supply of 2 W. and a corresponding drop of 10° C. across the shell. The temperature-interval across the outer brass casing being of the order of 0·001° C. was negligible. The drop of temperature within the inner sphere, being proportional to the observed temperature interval, involved an increase of only one part in 500 in the value of the thermal conductivity deduced from equation (5).

Since the potential leads used in determining the power supplied to the system were connected to the current wires outside the sphere and not directly to the lamp itself, the measured power was slightly in excess of that expended within the lamp. The resistance of the latter being about 12 ohms and that of the leads within the sphere 0·01 ohm, the correction involved was only 1 part in 1000 and was negligible.

A small uncertainty was involved in estimating the temperature of the outer brass casing by the use of a thermocouple immersed in the thermostat. This position of the couple was essential to preserve adequate insulation of the wires, to avoid error due to heat-conduction along them and to enable easy removal for calibration. Assuming a stagnant layer of water as great as 1 mm. in thickness to cover the surface of the mould, the error produced in the final conductivity result would have been of the order of 0·7 per cent, the presence of the boss reducing the error. Since it is unlikely that with the rapid rate of stirring adopted any stagnant film present was more than a small fraction of 1 mm. thick the probable error involved, being only a few parts in a thousand, was negligible.

§ 5. TEST OBSERVATIONS

Observations carried out with a single-lead system, with various power-supplies at the same effective temperature of experiment but with the inner thermocouple located on opposite sides of the inner sphere, gave the results shown in table 1. Agreement to a few parts in 600 was obtained between the values of apparent conductivity corresponding to a given power-supply.

Table 1.

Couple side *A*				Couple side *B*			
Mean temperature (° C.)	Watts	Temperature interval (° C.)	Apparent conductivity (c.g.s. × 10^{-3})	Mean temperature (° C.)	Watts	Temperature interval (° C.)	Apparent conductivity (c.g.s. × 10^{-3})
30·0	3·378	17·59	$0{\cdot}60_9$	30·1	3·439	18·03	$0{\cdot}60_5$
30·2	2·030	10·58	$0{\cdot}60_9$	29·9	2·042	10·62	$0{\cdot}61_0$
29·7	1·393	7·22	$0{\cdot}61_2$	30·5	1·338	6·92	$0{\cdot}61_4$

A further set of readings was made to test experimentally the method of eliminating the heat-loss at temperatures of experiment up to 80° C. A series of observations was first taken with a single-lead system, the temperature of the thermostat being adjusted to give several groups of readings such that in each group the power-supply varied while the effective temperature of experiment was

Table 2.

Mean temperature of experiment (°C.)	Lead system (single or double)	Ordinal number of experiment	Power-supply (W.)	Observed temperature-interval (°C.)	Apparent conductivity (c.g.s. $\times 10^{-3}$)	Heat-loss along leads (%)	Corrected conductivity (c.g.s. $\times 10^{-3}$)
4·0	S	10	1·543	7·85	0·624	1·1	$0{\cdot}61_8$
4·0	D	20	1·586	7·98	0·631	2·2	
8·3	S	9	3·224	16·54	0·619	2·3	$0{\cdot}60_5$
8·3	D	19	3·302	16·53	0·634	4·6	
30·9	S	11	3·184	16·77	0·603	2·2	$0{\cdot}59_1$
30·6	D	21	2·786	14·26	0·620	4·8	
29·9	S	2	2·042	10·62	0·610	2·3	$0{\cdot}59_6$
30·2	D	12	2·033	10·31	0·626	4·8	
30·5	S	1	1·338	6·92	0·614	2·6	$0{\cdot}59_8$
30·5	D	22	1·383	6·97	0·630	5·1	
43·5	S	25	2·373	12·52	0·601	3·2	$0{\cdot}58_3$
43·3	D	23	2·412	12·33	0·621	6·3	
55·7	S	3	3·356	17·99	0·592	2·9	$0{\cdot}57_6$
55·4	D	13	3·155	16·35	0·612	6·0	
55·1	S	7	2·294	12·27	0·593	3·2	$0{\cdot}57_5$
55·4	D	15	2·230	11·50	0·615	6·7	
54·7	S	4	1·445	7·57	0·606	4·1	$0{\cdot}58_2$
54·9	D	18	1·368	6·84	0·636	8·6	
67·2	S	26	2·454	13·13	0·593	3·9	$0{\cdot}57_1$
67·6	D	24	2·382	12·18	0·620	8·1	
80·1	S	5	3·280	17·97	0·579	4·0	$0{\cdot}55_7$
80·1	D	16	3·044	15·90	0·608	8·6	
79·7	S	8	2·255	12·26	0·583	5·3	$0{\cdot}55_3$
79·4	D	14	2·203	11·27	0·620	11·0	
79·5	S	6	1·451	7·70	0·598	7·0	$0{\cdot}55_7$
79·4	D	17	1·458	7·16	0·646	13·9	

practically constant. A corresponding series of experiments was then performed with a double-lead system. The method of pairing the observations to eliminate the heat-loss is indicated in the summarized table of data, table 2. The intermediate readings at 43° and 67° were taken with new plug castings. All the measurements were made with the inner thermocouple located in side *B* of the inner brass sphere.

The results show agreement to 1·5 per cent between individual values of the thermal conductivity of the casting obtained for the same mean temperature of

experiment by using power-supplies varying up to nearly 2·5 times the smallest value. This degree of agreement was taken as experimentally substantiating the method of eliminating the heat-loss, in view of the fact that in experiments at the highest mean temperature of observation, for which the heat-loss was greatest, there was no systematic variation of final results with power-supply. The results also justified the neglect of the small surface-loss from the top of the neck of the casting. The increase of heat-loss at the higher temperatures of experiment was probably due to the fact that the temperature of the portions of the leads just outside the plug was largely determined by the atmospheric temperature; this being so, for a given power-supply the temperature-gradient along the leads became greater since the lamp was hotter at the higher temperatures, and an increased heat-loss resulted.

The mean density of the casting was determined by weighing, the masses of the components of the mould being known. The value so obtained was 1·90 gm. cm.^{3} Molten sulphur on solidifying forms monoclinic crystals. As the mass cools below 95° C. these pass into the rhombic form, which is the stable condition below that temperature at atmospheric pressure. During the process of transformation of crystalline structure, the density increases from 1·96, that of the monoclinic crystals, to 2·07, that of the rhombic variety. Hence although the sulphur employed was a specimen of the rhombic form, the maximum value obtainable for the mean density of such a casting was 1·96, the density in the monoclinic state. Thus the casting employed in the test observations possessed a mean density differing by 3 per cent from the maximum possible value. As far as could be ascertained by inspection of the orifice of the shell there appeared to be no corresponding defect in the casting. It was not possible to determine whether the fault was local or whether more or less uniformly distributed throughout the shell.

While therefore the series of test observations considered above were essential to the establishment of the method as applied to a given material, it was necessary in order to obtain absolute values of the thermal conductivity of sulphur to make a further set of experiments with a specimen more satisfactory as regards mean density.

§ 6. DETERMINATION OF THE THERMAL CONDUCTIVITY OF SULPHUR

In making the new casting the same mould system as before was used. As on previous occasions it had been found necessary to remove the last vestiges of sulphur from the spherical surfaces of the mould by means of pumice stone, paraffin oil was employed as a lubricant. In consequence, the shape-factor on redetermination was found to be very slightly reduced, the mould having been employed for several trial castings made intermediately between the two on which systematic observations were performed. The new value of the shape-factor was 75·2 cm., the relevant radii being 5·104 cm. and 2·754 cm. respectively. The casting process finally adopted was carried out as in the case previously described, with the exceptions that the initial working temperatures were lower and the cooling process

was made more protracted. The mould was heated to 135° C. and initially filled with liquid sulphur having a temperature of 127° C. By gradually reducing the current supplied to the electric heater the system was cooled after about 5 hours to 117° C. Solidification was complete after the lapse of a further 40 minutes. The casting so obtained was found to possess a mean density of 1·94 gm./cm.^{3}, which is within about 1 per cent of the maximum possible value.

The lamp and plug systems were assembled in a manner analogous to that adopted for the earlier experiments, and the general method of procedure was the same. A few minor modifications in the apparatus were however introduced. The small cavities employed to take up the expansion of the mercury at the top of the inner brass sphere were filled with glycerin. By keeping the top surface of the plug covered with this liquid the exclusion of air from the system was ensured. With the object of reducing the heat-loss along the lamp leads, thin copper wires (30 s.w.g.) were used, the effective cross-section of the current leads being thereby reduced to about a quarter of the previous value. In addition an attempt was made to regularize this heat-loss by controlling as far as possible the temperature of the portions of the leads immediately outside the sphere. The leads for a distance of roughly 6 cm. from the top of the plug were closely encased in a copper sheath made from pieces of strip the ends of which dipped into the thermostat water. This sheath is indicated by the outer dotted lines in figure 3 (*a*). The outside of the sheath was well lagged. The temperature of the leads just outside the sphere was thus made largely independent of the atmospheric temperature, being chiefly defined by the bath temperature and the current supplied to the system.

New thermocouple wires were used, the temperature-drop across the sulphur shell being roughly 10° C. both in the main experiments, which were carried out as formerly, and in the subsidiary experiments conducted to eliminate the heat-loss along the leads. This loss, being small (of the order of 1 per cent), could be multiplied a number of times without seriously disturbing the thermal distribution of the system. In the auxiliary experiments the loss was increased to six-fold. Each of the leads to the lamp consisted of six strands of 30 s.w.g. copper wire. It was necessary to use both of the thermocouple channels in the inner sphere, one to contain the couple itself and the other to receive the lower ends of six additional copper wires of size 36 s.w.g. The extra copper element was conveniently employed in place of five constantan wires, and provided sufficiently approximate compensation. A narrow vertical groove cut in the sulphur plug on the side opposite to the similar groove containing the couple elements accommodated these additional wires in their passage to the exterior of the apparatus.

With sextuple leads the equation giving the heat flow per second is

$$W_6/\mathcal{J} = K_6 S\theta_6 = KS\theta_6 + 6H \qquad \text{.....(8),}$$

in which $6H$ is the heat-loss and θ_6 and K_6 are the temperature-interval and apparent thermal conductivity respectively. This relation used in conjunction with the single-lead equation (1) gives θ_6, K_6

$$K = K_1 - (K_6 - K_1)\,\theta_6/(6\theta_1 - \theta_6) \qquad \text{.....(9),}$$

or approximately, since θ_1 and θ_6 are roughly equal,

$$K = K_1 - \tfrac{1}{5}(K_6 - K_1) \qquad \text{.....(10).}$$

Thus, owing to the multiplication of the heat-loss, a given inaccuracy in the value of the apparent conductivity of the specimen was, as regards the effect upon the final result, six times less important in the auxiliary experiments than in the primary ones. The data obtained when three different plug castings were used for the main observations are given in abridged form in table 3.

Table 3.

Single-lead system					Sextuple-lead system				
Effective temperature of experiment (° C.)	Temperature-drop across sulphur shell (° C.)	Apparent conductivity (c.g.s. × 10^{-3})	Ordinal number of experiment	Plug	Effective temperature of experiment (° C.)	Temperature-drop across sulphur shell (° C.)	Apparent conductivity (c.g.s. × 10^{-3})	Ordinal number of experiment	Corrected conductivity (c.g.s. × 10^{-3})
5·1	9·90	0·628	13	II	5·6	9·72	0·684	17	$0{\cdot}62_4$
5·1	9·77	0·633	14	II					
5·1	10·01	0·641	22	III					
25·4	10·21	0·617	3	I	25·0	10·05	0·668	20	$0{\cdot}61_3$
24·0	9·96	0·627	9	I					
30·1	10·33	0·619	23	III	—	—	—	—	$0{\cdot}61_0$
35·0	10·26	0·612	1	I	34·6	10·84	0·659	15	$0{\cdot}60_6$
34·7	10·03	0·618	8	I					
45·9	10·10	0·609	6	I	45·7	10·20	0·648	18	$0{\cdot}60_2$
45·8	10·20	0·608	7	I					
54·3	10·60	0·590	2	I	—	—	—	—	$0{\cdot}59_0$
54·6	10·28	0·604	11	II					
54·9	10·16	0·603	21	III					
64·7	10·57	0·585	4	I	65·1	10·54	0·640	16	$0{\cdot}58_0$
64·5	10·43	0·594	10	I					
85·2	10·82	0·574	5	I	84·8	10·37	0·629	19	$0{\cdot}56_8$
85·1	10·59	0·581	12	II					

A determination with the sextuple-lead system was taken at every temperature of experiment for which primary experiments had been made, with the exception of 30° C. and 55° C. in which cases interpolated values of K_6 were used for the deduction of the corrected conductivity K. This was justifiable since the auxiliary readings showed regular variation and were taken in indiscriminate order. The correction to the power-supply necessitated by the connexion of the potential leads to the current wires outside the sphere and not at the lamp itself amounted to 1 part in 300 in the main experiments. The power-supply was of the order of 2 W. The calculated heat-loss for the single-lead system was sensibly constant, being of the order of 1·5 per cent at each temperature of experiment.

As deduced from the above figures the variation with temperature of the thermal conductivity of the specimen may be represented by a straight line to which the readings in general conform to within 1 per cent. The results are supported by the observations on the test casting to the extent that the test values may be represented by a similar line of practically the same slope but lower by 2 per cent on the conductivity scale, consistently with the small difference in the mean density of the two castings.

The values of the thermal conductivity of sulphur derived from the mean line are the following:

Temperature (° C.)	Conductivity (c.g.s.)
5	$0{\cdot}00062_6$
20	61_5
40	60_2
60	58_8
85	57_0

the temperature-coefficient being $-0{\cdot}12 \times 10^{-2}$ per ° C.

§ 7. COMPARISON OF RESULTS WITH THOSE OF OTHER OBSERVERS

The extent to which the derived values are in harmony with those obtained by other investigators is indicated in figure 5. The dotted curve is a section of that deduced by Kaye and Higgins [6], who conducted an investigation into the thermal conductivity of sulphur at temperatures from 20° C. to 210° C. using a plate method similar to that previously employed by them to determine the conductivity

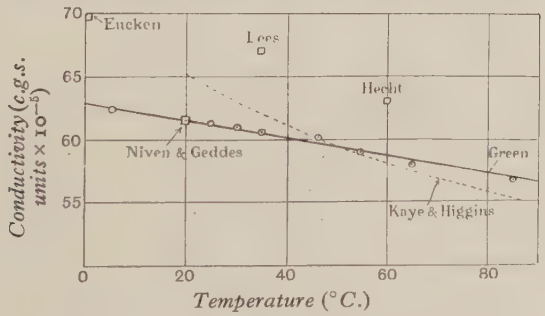

Fig. 5. Thermal conductivity of sulphur.

of liquids. The test layer was only 0·06 cm. thick and the temperature drop across it 4° C., a load being applied to the specimen to secure consistent results. The corrections involved appear to have amounted to some 10 per cent in all. The variation so obtained of the conductivity with temperature was non-linear and more rapid than that indicated by the present experiments, but there is agreement between the values of the conductivity as determined by the two methods at 50° C.

The other values indicated in the figure show rather large divergences among themselves. In addition to the result given, Lees[7] obtained an earlier value 0·00045 for sulphur at 15° C. Eucken[8] worked in the range - 190° C. to 0° C. Hecht[9], having made determinations for a number of poor conductors by an application of Neumann's method, gives the value for the conductivity of sulphur among the less accurate results. The value 0·000615 at a temperature in the vicinity of 20° C. obtained by Niven and Geddes[10] with a central hot vane between sulphur layers agrees well with that derived by the spherical shell method. The observed variation of conductivity with temperature, being linear, is analogous to that exhibited by other poor conductors. The crystals in sulphur castings appear in general to be too small for possible bias in axial orientation to affect the results for the aggregate appreciably, except conceivably in the case of a thin layer.

§ 8. ACKNOWLEDGMENTS

For permission to conduct these experiments at the Imperial College of Science, and for very valuable suggestions regarding them the author is much indebted to the late Prof. H. L. Callendar, C.B.E., F.R.S. Thanks are also due to Mr W. J. Colebrooke for facilitating the manufacture of the apparatus in the Physics Workshop and to Mr C. Hellary for the care taken in the constructional work.

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DISCUSSION

Dr Ezer Griffiths. I should like information on the following points from Mr Green. (1) Is there any possibility of a gas film between the sulphur shell and the metal walls? It is difficult to see how thermal contact is ensured at all temperatures, in view of the fact that the coefficients of thermal expansion differ very considerably. (2) Can it be assumed that a random distribution of sulphur crystals is being studied?

AUTHOR'S reply. Strong evidence against the existence of a gas film between the sulphur and the brass walls of the mould is furnished by the extreme tenacity with which the sulphur adhered to the metal. It was never possible to detach the outer casing without melting out the sulphur. In tests conducted at the conclusion of the conductivity measurements, with the system at laboratory temperature, all attempts to unscrew the upper hemisphere were unsuccessful, even when that hemisphere was subjected to violent knocking.

As far as can be ascertained by inspection, sulphur castings show an absence of directional bias in the orientations of the component rhombic crystals, the very small size of which is indicated by the opacity of the material even in thin layers. Further, such castings do not appear to give any definite cleavage directions on being broken. It is therefore a reasonable assumption that in the case of a specimen over 2 cm. in thickness a random distribution of crystals is being studied.

THE OPTICS OF PHOTOMETRIC MEASUREMENTS

By T. SMITH

Received December 12, 1931. *Read February* 19, 1932

ABSTRACT. The influence of the apertures which limit the light transmitted from the source to the photometer, and of the reflection and transmission coefficients of the specimen and apparatus used, including the source and the photometer themselves, on the quantities determinable from a photometric balance are considered. The way in which the apparatus is set up must take into account the precise information to be obtained. A general theory is given, which leads to the conclusion that in precise photometry the measurement of the light reflected in both directions, in addition to that transmitted, is necessary when the properties of materials are being determined. A suitable experimental arrangement for making the measurements is described. The method of calculating these quantities from the observations is given, and numerical examples are included.

§ 1. STATEMENT OF THE PROBLEM

In the normal work of an optical or photometric laboratory measurements are frequently required of the transmission factors of some materials and the reflecting factors of others. The measurements obtained are sometimes interpreted in a way which would be correct if no light were reflected in passing from the source to the observer's eye. The purpose of this paper is to indicate the significance of the photometric balance when reflected light is taken into account.

§ 2. OBSTACLES AND APERTURES

It is necessary in the first place to define every quantity we are concerned with in experimental work with some care, for its significance is slightly different from that of the similarly named quantity introduced in theoretical discussions on the properties of materials. In a typical measurement we are concerned with light which leaves a source of finite size and ultimately reaches the entrance window of a photometer. On the way it encounters various obstacles, including the specimen under examination and any lenses or mirrors used as experimental aids. To fix ideas we will suppose that all these materials are transparent and that the light we are interested in travels along paths grouped about a mean straight path from the source to the photometer. In confining our attention to this special case we are not limiting the general applicability of our conclusions.

It is important that all the light which reaches one side of the photometer should be derived from the appropriate source and should have traversed all the obstacles. To ensure this each obstacle is surrounded by a large opaque screen capable of absorbing all the light falling upon it. The obstacles and screens thus mark off a series of isolated spaces, and light can only pass from one space to the

next through the obstacle which serves as a window between the two. If then we are considering the transmission factor of a particular obstacle, this factor, in the absence of other limitations, will be defined for light which would pass through this obstacle and through the apertures in the two neighbouring screens left by the removal of the preceding and succeeding obstacles. Any light which impinges on any screen is lost, and we must recognize that the quantities we employ are to be interpreted as though such light had no existence. In many measurements the transmission factor relates to parts only of the obstacles. To find the effective portions we form in the space under consideration the optical images of all the apertures (i.e. the transparent obstacles) and of the source and the entrance pupil of the photometer, and determine the intersection with the obstacle of the largest cone which lies within all these images. This procedure is familiar in the theory of optical instruments. If the apertures effective in the determination of the cone change with small movements of the source or photometer the experimental arrangements are faulty and the interpretation of the measurements somewhat uncertain. As will be seen below, by the size of the source we may have to understand something larger than the incandescent body from which the radiant energy flows.

§ 3. REFLECTION FACTORS

We have not only to deal with directly transmitted light. Whenever light is refracted some is also reflected. To determine the meaning of reflection factor we should strictly construct the images of the different apertures by both reflection and refraction and thus determine the exact significance to be given to the term under the existing experimental conditions. In some cases this procedure might be unavoidable, but more frequently simple considerations show that we can only make trivial errors by assuming the effective apertures for the reflection factors to coincide with those for refraction. The chief point to bear in mind is that after a number of reflections the light has ultimately to be refracted through later apertures to reach the entrance pupil of the photometer, and thus after reflection it must normally lie within the cone for effective refracted rays.

With the determination of the limiting apertures, or alternatively of the limiting cone, the terms transmission factor and reflection factor assume definite significance. We have to note that for their meanings to be useful in other work the experimental conditions must be arranged to ensure that the illumination is reasonably uniform over the several apertures. The only other vital point to bear in mind is that a given obstacle has one transmission factor and two reflection factors*. In general all these are changed if the obstacle is reversed so that the directly incident light traverses it in the reverse direction. Only when the limiting cones for the spaces on the two sides of an obstacle are symmetrical can the factors remain unchanged on reversal.

* See "On the light transmitted and reflected by a pile of plates" and "Note on the immutability of transmissive factors with reversal of light," *Trans. Opt. Soc.* **27**, 31 (1925–6).

§ 4. ILLUSTRATION

The distinction between the two reflection factors, quite apart from the effect of the apertures, persists unless there is complete symmetry. As this is often not realized it may be helpful to give a simple example—in this case involving a broken path.

Let the obstacle consist of a refracting prism, on one side of which the light is incident normally while on the other the incidence is oblique. If the transmitted light travels in the direction $PABQ$, a certain fraction r_A of the incident light is reflected directly back to P from A and another fraction t_A enters the glass. When the light reaches B part is reflected in the direction BR and is to be regarded as lost, and another part, say the fraction t_B, is refracted to Q. Thus the total reflected light is measured by r_A and the total transmitted by $t_A a t_B$ where a differs from unity on account of the absorption of the material of the prism.

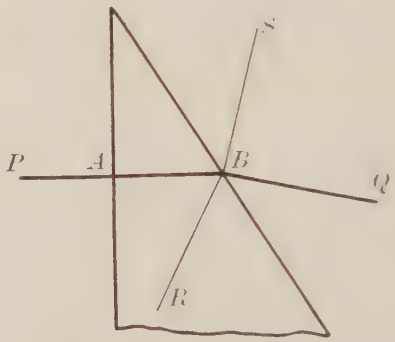

Fig. 1.

Now consider the corresponding factors when the light travels in the reverse direction from Q to P. When B is reached some of the light is reflected in the direction BS and lost, and the fraction t_B is refracted towards A. When A is reached the fraction t_A is transmitted and the fraction r_A reflected back towards B. On arrival at B the part reflected along BR is lost as before and the fraction t_B is refracted towards Q. Thus the total transmitted from Q to P is $t_B a t_A$, which agrees with the fraction transmitted from P to Q, and the fraction reflected back to Q is $t_B a r_A a t_B = r_A a^2 t_B^2$, which is less than r_A, the fraction reflected back to P; the two reflection coefficients are therefore in this case necessarily unequal. If the two surfaces of the prism were in a similar condition we should clearly have equality in the reflection coefficients (usually zero values, as the reflected light would probably strike a screen) we are at the moment considering if the prism were placed in the position of minimum deviation.

§ 5. MATHEMATICAL THEORY

We have now to consider how the factors so defined enter into an expression for the light entering the photometer. Let three successive obstacles, in the order in which they are encountered by directly transmitted light, be identified by the numbers $n-1$, n, $n+1$. Let I_n denote the total light falling on the effective aperture of obstacle n in the forward direction, and J_n that falling on it in the reverse direction. Let t_n be the transmission factor, and r_n and r_n' the reflection factors for light incident in the forward and reverse directions respectively. From these definitions we have the general equations

n, I_n
J_n
t_n, r_n, r_n'

$$I_{n+1} = I_n t_n + J_n r'_n,$$
$$J_{n-1} = J_n t_n + I_n r_n.$$

We may combine these results in the form

$$(J_n \quad -I_{n+1}) = (J_{n-1} \quad -I_n)\,\mu_n,$$

μ_n

where the matrix μ_n is given by

$$\mu_n = \begin{pmatrix} \frac{1}{t_n} & -\frac{r_n'}{t_n} \\ \frac{r_n}{t_n} & t_n - \frac{r_n r'_n}{t_n} \end{pmatrix},$$

so that $|\mu_n| = 1$. When there are l obstacles, numbered from 1 to l, we have

l

$$(J_l \quad -I_{l+1}) = (J_0 \quad -I_1)\begin{pmatrix} a & -b \\ c & d \end{pmatrix} = (J_0 \quad -I_1)\,\mu_1\mu_2 \ldots \mu_l,$$

where $bc + ad = 1$*. Here we must interpret I_{l+1} as the radiation falling on the

* If

$$\mu_1 = \begin{pmatrix} a_1 & -b_1 \\ c_1 & d_1 \end{pmatrix}, \quad \mu_2 = \begin{pmatrix} a_2 & -b_2 \\ c_2 & d_2 \end{pmatrix},$$

the product $\mu_1\,\mu_2$ is given by

$$\mu_1\,\mu_2 = \begin{pmatrix} a & -b \\ c & d \end{pmatrix},$$

where

$$\begin{aligned} a &= a_1a_2 - b_1c_2, \\ b &= a_1b_2 + b_1d_2, \\ c &= c_1a_2 + d_1c_2, \\ d &= -c_1b_2 + d_1d_2. \end{aligned}$$

When more than two matrices are to be multiplied together we may proceed by finding the product of two factors, and reapplying the formula with this product as one of the factors. Note that $\mu_1\,\mu_2$ is not equal to $\mu_2\,\mu_1$, so that the order of the factors is important. From the above equations it is easy to show that

$$(bc + ad) = (b_1c_1 + a_1d_1)\,(b_2c_2 + a_2d_2),$$

and the left side is equal to unity if both factors on the right have this value.
The equation

$$(P \quad Q) = (R \quad S)\begin{pmatrix} a & -b \\ c & d \end{pmatrix}$$

may be regarded as a method of writing the two equations

$$P = aR + cS, \qquad Q = -bR + dS,$$

and the solution of these equations when $bc + ad = 1$ is

$$R = dP - cQ, \qquad S = bP + aQ,$$

or

$$(R \quad S) = (P \quad Q)\begin{pmatrix} d & b \\ -c & a \end{pmatrix}.$$

photometer, and J_0 as the reflected radiation falling on the source or that part of the surrounding apparatus which lies within the effective cone of rays. In general both the source and the photometer reflect light. Let their reflection factors
s, p (corresponding to r_0' and r_{l+1}) be s and p respectively. Then the light incident on the first obstacle consists of that directly emitted by the source, which we will call i, and reflected light, i.e.

$$I_1 = i + J_0 s.$$

Also we clearly have $$J_l = I_{l+1} p.$$

The ratio ordinarily utilized in photometric measurements is the ostensible
T transmission factor $T = I_{l+1}/i$. From the above equations

$$\frac{I_{l+1}}{i} = \frac{J_0 b + I_1 d}{I_1 - J_0 s}$$

and

$$p = \frac{J_l}{I_{l-1}} = \frac{J_0 a - I_1 c}{J_0 b - I_1 d}.$$

The latter equation gives

$$\frac{J_0}{I_1} = \frac{c + dp}{a - bp},$$

so that

$$T = \frac{I_{l+1}}{i} = \frac{b(c + dp) + d(a - bp)}{a - bp - (c + dp)s} = \frac{1}{a - bp - cs - dps}.$$

This expression shows that the usual interpretation of a photometric balance may be seriously in error. In general we must know both p and s. If both are known to be small and the light reflected by the whole system of obstacles is also small we may neglect the terms involving b, c, d, since they are then second order quantities. Even when these conditions are satisfied we have only determined a, and this is insufficient to give the transmission factor of a particular obstacle unless no other obstacles are present. In the more general case we can only find the properties of a particular obstacle when we know the properties of each auxiliary obstacle and can make observations from which the a, b, c, d of the complete series of obstacles can all be determined.

We note that if the photometer and source are interchanged, and if the effective portions of the obstacles are thereby unchanged, the quantity measured by the photometric balance is

$$T' = \frac{J_0}{j} = \frac{1}{a - bs' - cp' - dp's'},$$

s', p' where s' and p' are the reflection factors of the source and the photometer in their new positions. If, as will often be the case, s' and p' are substantially equal to p and s respectively, no new information can be derived from the second measurement.

§ 6. REFLECTION MEASUREMENTS

Clearly there is only one way of obtaining the additional information required. We must arrange to have the source and the photometer on the same side of the
R series of obstacles and make measurements of the apparent reflection factors R

and R'. In taking these measurements the apparatus must be so contrived that the effective areas of the obstacles are unaltered, that the source and photometer do not interfere with one another, and that all the light falling on the photometer is received from the system under measurement. Let both photometer and source be situated before the first obstacle, and let q be their joint reflection factor. Also let u be the reflection factor of any objects at the other end of the system under examination. The ratio to be measured is then J_0/i' under the conditions

R'

u

$$I_1 = i' + J_0 q, \quad J_l = I_{l+1} u.$$

This is readily found to give

$$R = \frac{J_0}{i'} = \frac{c + du}{a - bu - cq - dqu}.$$

Similarly let q' be the joint reflection factors of the source and photometer when placed behind the last obstacle, and u' the reflection factor of objects before the first obstacle. The conditions are $J_l = j' + I_{l+1} q'$, $I_1 = J_0 u'$, giving

$$R' = \frac{I_{l+1}}{j'} = \frac{b + du'}{a - bq' - cu' - dq'u'}.$$

We now have five equations connecting a, b, c, d, viz. the expressions for T, T', R, R' and the identity $bc + ad = 1$. From a suitable set of four we can determine a, b, c, d, and thence determine the properties of a single obstacle under the conditions of the experiment.

It is not difficult to arrange the apparatus so that

$$p = s' = q' = u, \text{ and } p' = s = q = u'.$$

The equations then give $T = T'$,

$$\begin{aligned} a &= (1 + uR')(1 + u'R)/T - uu'T, \\ b &= (1 + u'R)R'/T - u'T, \\ c &= (1 + uR')R/T - uT, \\ d &= T - RR'/T. \end{aligned}$$

These results are best expressed in the form

$$\begin{pmatrix} a & -b \\ c & d \end{pmatrix} = \begin{pmatrix} 1 & u' \\ . & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{T} & -\frac{R'}{T} \\ \frac{R}{T} & T - \frac{RR'}{T} \end{pmatrix} \begin{pmatrix} 1 & . \\ -u & 1 \end{pmatrix},$$

where the matrix involving the experimental measurements corresponds in form to the matrix expressing the properties of an individual obstacle. If the purpose of the measurements is to determine the properties of obstacle n, we obtain

$$\mu_n = M_{1,n-1} \begin{pmatrix} 1 & u' \\ . & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{T} & -\frac{R'}{T} \\ \frac{R}{T} & T - \frac{RR'}{T} \end{pmatrix} \begin{pmatrix} 1 & . \\ -u & 1 \end{pmatrix} M_{n+1,l},$$

where $M = \begin{pmatrix} d & b \\ -c & a \end{pmatrix}$, and the suffixes refer to the extreme obstacles in the products of the μ's for which a, b, c, d are to be computed.

§ 7. EXPERIMENTAL ARRANGEMENTS

The theoretical considerations we have been investigating help us to realize what kind of experimental arrangement is desirable in making tests. The arrangement shown in figure 2 is suitable when the photometer occupies only a small portion of the illuminated field. The obstacles are arranged in their correct positions

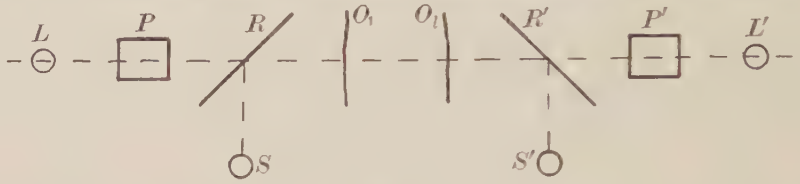

Fig. 2.

on a photometric bench and at each end is placed a photometer P, P'. The comparison lamps by which a photometric balance is obtained are denoted by L, L'. It is important that no other parts of the apparatus but L and L' should be moved, for then the effective apertures will be the same for all the observations. The systems are viewed by the photometers through windows cut out of reflectors R, R', which are used to reflect light from sources S, S' into the system. Readings with the photometer P and comparison lamp L are made

(1) when S is on and S' and L' off,

(2) when S' is on and S and L' off;

and similar readings are made with photometer P' and comparison lamp L'

(3) when S' is on and S and L off,

(4) when S is on and S' and L off.

§ 8. OPAQUE MATERIALS

The modifications required in the apparatus when reflecting rather than refracting obstacles are present are sufficiently obvious. The theory is simpler, inasmuch as we then have a single reflection coefficient and no transmission coefficient for such obstacles. A word should, however, be said about measurements on matt surfaces. In some respects the considerations resemble those for reflecting surfaces, but the size of the specimen is of much importance. Particular care should be taken to see that the extent of the specimen illuminated and that visible from the photometer correspond to the measurements significant in the application of the results obtained.

§ 9. NUMERICAL EXAMPLES

The following examples are intended to illustrate the numerical calculations required according to the foregoing theory and to indicate for typical experimental measurements the magnitude of the discrepancy between results computed according to this theory and to the current approximate theory.

(1) We readily see that in the direct photometry of lamps the reflection factors of the lamp and of the photometer may safely be neglected. For if we assume that

the minimum separation between the lamp and photometer is 50 cm., the area of the hemisphere of this radius is about 15,000 cm.^{2} If the photometer has a diffusing surface, the light falling upon it will be scattered in all directions. If the intensity of this light scattered in the direction of the lamp were twice that of the mean for equal areas on the hemisphere the light falling on a lamp of 100 cm. projected area would only be 1·3 per cent of that falling on the photometer screen. If the lamp scattered the light falling on it in the same way as the photometer screen, and the area of the latter were as great as that assumed for the lamp, the doubly reflected light falling on the photometer screen would be less than 0·02 per cent of that directly incident. With the smaller screen size of real photometers this fraction would be reduced. The effects are therefore entirely negligible.

As another example consider a photometer which reflects 10 per cent of the incident light specularly. The reflected light is equivalent to a lamp rated at 10 per cent of the real source placed at the same distance as the latter from the photometer, but on the opposite side. The light reflected back to the lamp is thus $2\frac{1}{2}$ per cent of that incident on the photometer. In the most unfavourable case this will be scattered as in the previous example, and the effects are again entirely negligible.

(2) In many measurements the reflected light is by no means negligible. An example is afforded by the derivation of reflection factors from measurements of light transmitted. Unless special arrangements are made the direct measurement of reflection factors is not easy. These difficulties are often increased by the small amount of light reflected. The transmission measurement is simpler, but the uncertainty in the measurement is considerable because the reflection factor is derived from the difference between two slightly different measurements. Thus if the reflection factor of the polished surface of glass is to be measured, a plate of glass will be used, and if the required factor is of the order of 4 per cent the transmission for the plate will be about 92 per cent. An error of 1 per cent in the measurement of the latter corresponds to an error of more than 12 per cent in the reflection factor. To increase the accuracy several similar plates may be arranged in series, and the usual theory will then lead to an erroneous result. By way of illustration let us suppose that no light is lost, so that the sum of the reflection and transmission coefficients is unity. Putting $r/t = r'/t = x$, we find

$$\begin{pmatrix} \frac{1}{t} & -\frac{r'}{t} \\ \frac{r}{t} & t - \frac{rr'}{t} \end{pmatrix} = \begin{pmatrix} 1+x & -x \\ x & 1-x \end{pmatrix}.$$

Moreover, by the multiplication rule,

$$\begin{pmatrix} 1+x_1 & -x_1 \\ x_1 & 1-x_1 \end{pmatrix}\begin{pmatrix} 1+x_2 & -x_2 \\ x_2 & 1-x_2 \end{pmatrix} = \begin{pmatrix} 1+x & -x \\ x & 1-x \end{pmatrix},$$

where $x = x_1 + x_2$. Thus when there is no loss of light the quantities r/t are simply additive, and the order of the obstacles is insignificant unless a rearrangement modifies the assumed conditions.

Now suppose that in the absence of any loss of light n similar obstacles are placed in series. The measurable transmission factor T is connected with the individual reflection factor r by the equation

$$\frac{1}{T} = 1 + nx = 1 + \frac{nr}{1-r}.$$

According to the approximate theory sometimes adopted the relation is

$$T_1 = (1 - r_1)^n.$$

It will not escape notice that the exact expression is the simpler of the two for numerical computation. For $n = 1$ the two expressions agree, but they differ for other values of n. For example, if $r = r_1 = 4$ per cent we obtain the following values:

n	2	4	8	12	24
T	0·923	0·857	0·750	0·667	0·500
T_1	0·922	0·849	0·721	0·613	0·375

Clearly with as few as two plates ($n = 4$) the error due to the incorrect theory is of the same order as the photometric uncertainty, and increases rapidly as more plates are used. We may exhibit the theoretical error in another form, by finding the value of r_1 that would be deduced from exact observations when the real value of r is 4 per cent. They are as follows:

n	2	4	8	12	24
$100r_1$	3·92	3·78	3·53	3·32	2·85

These results indicate that even in very simple systems it is important to employ the exact theory.

(3) The comparison given above is unduly favourable, for in measurements of this type the light reflected by the photometer should be taken into account. Let us suppose that the reflection factor of the photometer is 10 per cent, and that of the source negligible. With the same plates as before the value of T will be given by

$$\frac{1}{T} = a - bu = 1 + x - x/10 = 1 + 0{\cdot}9x.$$

The numerical values of T, together with the values of r_1 derived from them according to the approximate theory, are given in the following table. The extent of the departures from the correct value of 4·00 per cent for r_1 show that it is essential to take the reflection factor of the photometer into account.

n	2	4	8	12	24
T	0·9302	0·8696	0·7692	0·6896	0·5263
$100r_1$	3·55	3·43	3·23	3·05	2·64

It may be observed that the percentage inaccuracy increases with r, and that the ordinary theory is now incorrect even for $n = 1$.

This example shows that the introduction of even a single thin sheet of glass may vitiate the simplest deductions derived on the usual theory from photometric

measurements. Still more erroneous conclusions may be drawn when two or three optical parts such as lenses and filters are traversed by the light.

(4) A simple measurement not infrequently required is the determination of the transmissivity of a given material. The value is derived from the transmittance of a suitably prepared specimen of known dimensions. As a rule the refractive index of the material will be known, and if the surfaces are freshly polished the surface effects can be computed from Fresnel's formula. The experimental conditions are usually arranged so that light passes normally through the surfaces, and the losses that take place may be attributed entirely to absorption. It is easy to show that if τ is the transmittance, and the ratio r/t for each surface is equal to x, the matrix for the specimen is

$$\begin{pmatrix} a & -b \\ c & d \end{pmatrix} = \begin{pmatrix} 1+x & -x \\ x & 1-x \end{pmatrix} \begin{pmatrix} \tau^{-1} & 0 \\ 0 & \tau \end{pmatrix} \begin{pmatrix} 1+x & -x \\ x & 1-x \end{pmatrix}.$$

Let us suppose the refractive index is 1·5. Then

$$x = \frac{(1{\cdot}5-1)^2}{4\times 1{\cdot}5} = \frac{1}{24},$$

$$\begin{pmatrix} a & -b \\ c & d \end{pmatrix} = \begin{pmatrix} \frac{25}{24} & -\frac{1}{24} \\ \frac{1}{24} & \frac{23}{24} \end{pmatrix} \begin{pmatrix} \tau^{-1} & 0 \\ 0 & \tau \end{pmatrix} \begin{pmatrix} \frac{25}{24} & -\frac{1}{24} \\ \frac{1}{24} & \frac{23}{24} \end{pmatrix}$$

$$= \begin{pmatrix} \frac{25}{24\tau} & -\frac{\tau}{24} \\ \frac{1}{24\tau} & \frac{23\tau}{24} \end{pmatrix} \begin{pmatrix} \frac{25}{24} & -\frac{1}{24} \\ \frac{1}{24} & \frac{23}{24} \end{pmatrix},$$

or

$$a = \frac{(625\tau^{-1}-\tau)}{576},$$

$$b = c = \frac{(25\tau^{-1}+23\tau)}{576},$$

$$d = \frac{(-\tau^{-1}+529\tau)}{576}.$$

If the simplest equipment is used for these measurements we shall have to deal with such values of u and u' as 0·1 and zero. Assuming these, the relation for finding τ becomes

$$T = \frac{576}{\{625\tau^{-1}-\tau-0{\cdot}1\,(25\tau^{-1}+23\tau)\}}$$

$$= \frac{576}{(622{\cdot}5\tau^{-1}-3{\cdot}3\tau)}.$$

Taking in turn (i) 0·80 and (ii) 0·20 as measured values of T, we compute corresponding values of τ, using the first term in the denominator to obtain first approximations:

(i) $\tau \simeq 0{\cdot}80 \times 622{\cdot}5/576 = 0{\cdot}8646,$

(ii) $\tau \simeq 0{\cdot}20 \times 622{\cdot}5/576 = 0{\cdot}2161.$

Inserting these in the second denominator term we obtain the corrected values

$$\text{(i)}\ \tau = 0{\cdot}8612, \qquad \text{(ii)}\ \tau = 0{\cdot}2161,$$

showing that the second term is only significant for the more transparent material. We may compare these values with those given by the common formula

$$T = \tau\,(1 - 0{\cdot}04)^2;$$

these are $\text{(i)}\ \tau = 0{\cdot}8681, \qquad \text{(ii)}\ \tau = 0{\cdot}2170.$

With the more transparent material the difference would not usually be considered negligible.

It would be easy to multiply examples and thus show that in more elaborate measurements, such as those made with some spectrophotometers, the application of an inexact theory may lead to much greater errors than those already illustrated. The examples given have been confined intentionally to measurements where it has been possible to avoid the direct measurement of reflection factors. The less simple determinations are probably not of general interest, and will tend to be regarded as tasks for specialists, who should themselves be capable of a critical examination of the procedure followed. It will therefore suffice to add a single caution. The exact significance of the quantities entering into the equations must be studied. Thus the "ostensible transmission factors" are not necessarily the ratios determined from measurements with and without a specimen. For example, this will not be the case if neither the reflection factor for the source nor that for the photometer is negligible. For assuming we are testing a specimen in which there is no loss of light, employing the variable x to denote its properties, we have

$$T = \frac{1}{1 + x - (u + u')\,x - uu'\,(1 - x)}$$

$$= \frac{1}{1 - uu' + x\,(1 - u)\,(1 - u')}.$$

A measurement made when the specimen is removed is represented by putting $x = 0$, and the corresponding value of T is not unity but T_0, where $T_0 = (1 - uu')^{-1}$. The quantity determinable from observation is usually T/T_0.

SOME PRINCIPLES GOVERNING THE DESIGN OF KERR CELLS

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Communicated by Dr W. H. Eccles, F.R.S., December 22, 1931.
Read and discussed February 19, 1932

ABSTRACT. The paper describes some principles that were employed in designing a Kerr cell for use in a television system. The volts/intensity characteristic of the cell is developed and the theory is extended to apply to the case when an optical bias is used. The chromatic effects obtained with high potentials are discussed and finally the treatment of the cell as an integral part of an optical system is given. It is shown that from this aspect the most efficient form of cell is one using shaped plates. The frequency-response is briefly discussed.

§ 1. INTRODUCTION

In recent years a great deal of attention has been directed towards the development of methods of modulating a light-source, more particularly in connexion with recording sound on film, transmission of pictures by wire or wireless and television. Generally speaking, the two main requirements are (*a*) a good over-all frequency-response and (*b*) the power to handle as large a flux of light as possible. The frequency range varies according to the use to which the modulating device is to be applied, and the amount of light required also is dependent on the application in view; for instance, a photographic record may be required or the result may be viewed directly by the eye. Again, the choice of a suitable device depends on the circumstances under which it is to be used: if a picture is to be projected in a hall, the use of an arc lamp can be contemplated; for other purposes it may be essential to keep the light-intensity constant, in which case an arc lamp would be distinctly undesirable. Whatever the purpose, however, the demand is usually made for higher frequency-response and more light, and the development of a Kerr cell for use in projecting a television picture has followed these lines. The principles on which this development has been based at the laboratories of The Gramophone Company are described in this paper.

§ 2. THEORY OF A SIMPLE KERR CELL

The effect which is used in the Kerr cell was first observed by Dr Kerr in 1875*. He found that certain substances became doubly refracting when subjected to an electric stress, so that a plane-polarized beam of light, on passing through the

* J. Kerr, *Phil. Mag.* 1, 337–446 (1875).

strained medium, became elliptically polarized. A simple form of apparatus is shown diagrammatically in figure 1. Light from an arc is focussed by L_1 on to the Kerr cell K after the light has been plane-polarized by the nicol N_1. On the far side of K is the analysing nicol N_2. The cell itself consists of a bath of nitrobenzene in which two parallel metal plates are immersed at a small separation. The nicols are set in the crossed position, with the polarizing planes at 45° to the direction of the electric stress that exists in the nitrobenzene when a potential is applied between the two immersed plates.

The light incident on the cell is plane-polarized by N_1, but owing to the double refraction occurring in the Kerr cell, a phase retardation is introduced between the components parallel and at right angles to the electric stress. The light on emerging from the cell is therefore elliptically polarized and has a component that can be transmitted by the second nicol N_2. The intensity of the transmitted light can be readily calculated* and the results are briefly summarized below.

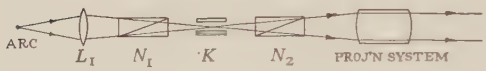


Fig. 1. Optical system for use with Kerr cell.

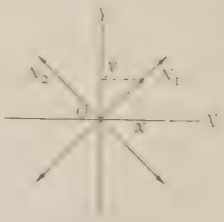


Fig. 2.

In figure 2 the vector ON_1 represents the light incident on the Kerr cell; OX, OY represent the stress directions in the nitrobenzene and ON_2 the plane of the light transmitted by N_2. ON_1 has components Ox, Oy in the X, Y planes and these components will travel with slightly different velocities owing to the double refraction. On emerging from the stressed medium there will be a phase retar-

ϕ dation ϕ given by

$$\phi = Kl\,(E/d)^2 \qquad \ldots\ldots(1),$$

l, E where l is the length of the light path in the strained medium, E the potential applied
d, K across the Kerr cell plates, d the separation between the plates and K a constant depending on the medium subjected to the stress and on the wave-length of light under consideration.

I Straightforward calculation then gives the value of the intensity I of the light transmitted by the second nicol thus:

$$I = a^2 \sin^2 \tfrac{1}{2}\phi \qquad \ldots\ldots(2)$$

$$= a^2 \sin^2 [\tfrac{1}{2}Kl\,(E/d)^2] \qquad \ldots\ldots(3),$$

a where a corresponds to the amplitude of vibration when I is a maximum. For a

* See "Kerr cell method of recording sound," *Trans. Soc. Motion Picture Engineers*, **12**, 748 (1928).

cell of given dimensions in which l and d are fixed, the relation between light intensity and applied potential becomes

$$I = a^2 \sin^2 K_1 E^2 \qquad \text{.....(4),}$$

K_1 being another constant. K_1

From figure 3, which represents this relation diagrammatically, various conclusions may be drawn. For sound recording the relation between intensity and voltage must be linear or very nearly so: to attain this result the portion AB of the curve is used. This necessitates a constant biasing potential corresponding to the point C and modulation between the limits set by A and B. In this way a practically undistorted sound-record can be made.

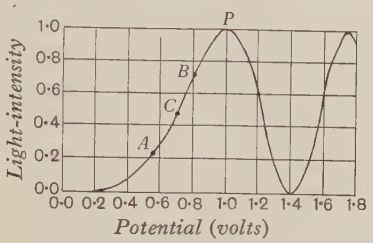


Fig. 3. Kerr-cell characteristic curve.

For television the no-distortion criterion must be very largely neglected. At B the intensity is little more than three times that at A, so that the normal contrasts between light and shade of a picture, which may be 100 or 1000 to 1, would fail altogether to be reproduced were this portion of the curve alone utilized. It is therefore necessary, in television reproduction, to modulate over a rather longer portion of the curve, say between potentials of 0·2 and 1·0 in figure 3, with a biasing voltage of 0·6. This will give a greatly increased contrast to the picture, but owing to the pronounced curvature of the characteristic the light and shade will not be accurately reproduced. The error, fortunately, is one to which the eye is not highly sensitive.

§ 3. USE OF AN OPTICAL BIAS

The difficulty referred to above is due in particular to the small change in intensity for a given voltage-change at the low-intensity end of the curve. If we suppose that by some suitable means the Kerr effect corresponding to the point P can be neutralized, then P would be the zero-intensity point and O the point of maximum intensity. In practice all that is required to neutralize the Kerr effect at P is the introduction of an optical retardation of a half wave-length between the nicols N_1 and N_2, figure 1, in the orientation necessary to oppose the retardation in the Kerr cell. That this is correct is evident from equation (2) above, for the first intensity maximum P will occur when $\phi = \pi$ which, of course, is a half-wave-length retardation. The equation giving the intensity relation for the combined Kerr cell and optical bias is thus:

$$\begin{aligned} I &= a^2 \sin^2 \tfrac{1}{2}(\phi - \pi) \\ &= a^2 \sin^2 (K_1 E^2 - \tfrac{1}{2}\pi) \end{aligned} \qquad \text{.....(5).}$$

This curve is plotted in figure 4 and it will be realized that it is of the same shape as that in figure 3 except that it is inverted. The advantage of this new characteristic over the old is the steeper slope at the low-intensity portion of the curve, so that a given potential-change on the Kerr-cell plates will produce a much greater proportional intensity-change than before. For example, with a biasing potential of 0·8 a very satisfactory picture could be produced by modulating between 0·6 and 1·0. This is only half the modulation previously required. Actually the modulation can be made still smaller as the visually significant quantity is not the intensity I itself but log I. This means that the upper half of the characteristic curve is of very much less importance than the lower half.

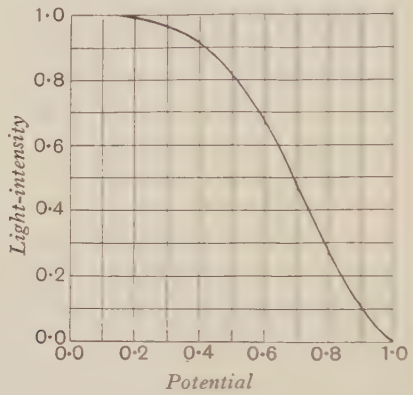


Fig. 4. Characteristic curve for Kerr cell with optical bias of $\frac{1}{2}\lambda$.

Apart from the advantage of a smaller modulating voltage, a useful point in itself, a gain in definition of the televised picture should also be obtained, inasmuch as the use of a final step-up transformer with its attendant distortion, due to phase-shift and frequency-attenuation, may be avoided. A still greater improvement should result from the more nearly linear relation between voltage and intensity that is obtained with an optical bias.

The method of applying this result is apparently quite simple, although what might appear as the simplest method does not, in practice, prove to be so. All that is needed is a piece of mica or other doubly refracting substance of just the thickness necessary to produce a half-wave-length retardation. This is not easy to obtain, and when it is available some strain in the glass walls of the vessel containing the Kerr cell is liable to upset all calculations. The more satisfactory method is to introduce a piece of clear celluloid held in a device with which it can be subjected to a strain sufficient to make it doubly refracting and thus produce the required retardation. With this arrangement it is, of course, very easy to allow for any strains already existing in intermediate glass surfaces.

§ 4. USE OF HIGH BIASING POTENTIAL

An alternative method of obtaining a straighter characteristic is to use a high biasing potential of, say, 1·2 (see figure 3) and modulate between 1·0 and 1·4. At first sight this would appear to give satisfactory results as the curve deviates from a straight line by only small amounts and the necessary modulating potential is greatly reduced. Unfortunately chromatic dispersion becomes of increasing importance as the biasing potential is raised. The formula (1) for ϕ contains a constant K which varies inversely as the wave-length of light considered, so that the shorter the wave-length the greater the phase-difference introduced. This is shown in figure 5 where the volts/intensity curves for three wave-lengths are given. This shows very clearly that where, for instance, the red is a minimum, at a potential of 1·3, the green and blue are nearly at a maximum with a blue-green as the resultant colour for that potential. Again, at the green minimum, both the red and blue have finite values with the resultant colour a purple. At the blue-minimum the colour is a yellow or reddish brown. An accurate analysis of the colour effects would require several more curves taken for wave-lengths at closer intervals throughout the spectrum, in addition to the absorption curve of the nitrobenzene. Figure 5, however, is sufficient to indicate the nature of the phenomenon. Practical confirmation of the above was obtained on a particular Kerr cell with the results given in the table.

Potential on Kerr-cell plates (volts)	Colour observed	Estimated intensity (arbitrary units)
1200	Greenish white	100
1300	Yellow	50
1400	Reddish yellow	25
1450	Orange	15
1500	Orange pink	10
1550	Pink	15
1600	Pinkish white	20

The estimated intensity cannot be regarded in the light of an accurate measurement, but merely as a rough indication. The evidence is sufficient, however, to show that for ordinary purposes a Kerr cell cannot be operated successfully on the steeper slopes of its characteristic, although there might be a very definite and useful application for television in colours.

The chromatic dispersion, of course, exists at even low potentials, but as the effect is additive no result is noticeable at low voltages, as can be seen from figure 5. The first upward slopes of all three curves are very nearly the same, the blue-maximum being reached slightly before the red.

As a theoretical problem it is interesting to consider the possibility of correcting for the chromatic dispersion in some way analogous to the achromatizing of a lens. The problem is very definitely academic and of no practical importance, but it may be pointed out that the only possibility would appear to be to use two Kerr

cells containing different liquids and to make use of their different refractive chromatic dispersions. This dispersion, which is connected with refractive index, must be distinguished from the Kerr chromatic dispersions which would always remain proportionately the same whatever liquids were used. The use of right- or left-handed quartz is of no value, since the net result would be that for most wave-lengths the Kerr cell would no longer be between crossed nicols.

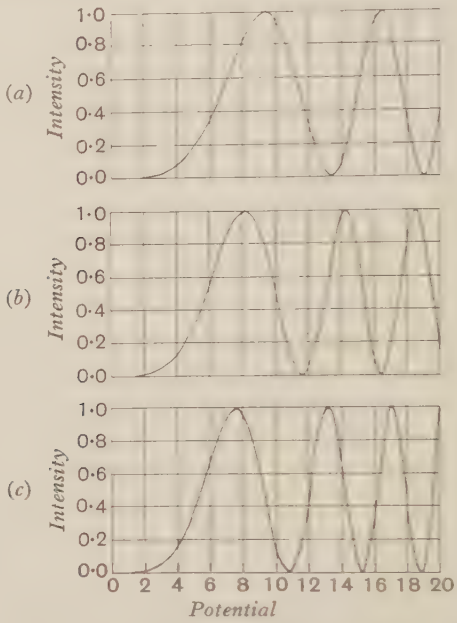


Fig. 5. Kerr-cell characteristic curves for three wave-lengths. (*a*) $\lambda = \cdot 70\mu$ (red); (*b*) $\lambda = \cdot 53\mu$ (green); (*c*) $\lambda = \cdot 46\mu$ (blue).

§ 5. KERR CELLS WITH SHAPED PLATES

In designing a Kerr cell it is necessary to consider it as part of the optical system by which the television picture is being projected. In this system, a given small area or spot of light is required to radiate within a given cone, the actual dimensions of spot and cone being determined by such optical constants of the system as aperture and focal length.

Suppose that, for the system with which we are dealing, the area and cone of light required are as shown in figure 6 (*a*). Then to satisfy these requirements with a parallel-plate Kerr cell, the plates would have to be as shown in (*b*) although their length and separation could be varied somewhat. Obviously, however, the arrangement shown in (*c*), in which the plates are shaped so as to fit the cone, is the more efficient form since the separation between the plates is at each point the narrowest that will still allow the required cone of light to be transmitted. At each point, therefore, the Kerr effect is a maximum for a given potential and the total retardation is also a maximum.

The expression (1) for ϕ shows that l must be large and d small if ϕ is to be of a useful magnitude and E is not to be excessive. With l long and d small, in a parallel-plate Kerr cell, the cone of light transmitted must necessarily be very limited. With the shaped plates l can be increased indefinitely without cutting down the cone of light, although the gain is eventually counterbalanced by the increased absorption in the nitrobenzene.

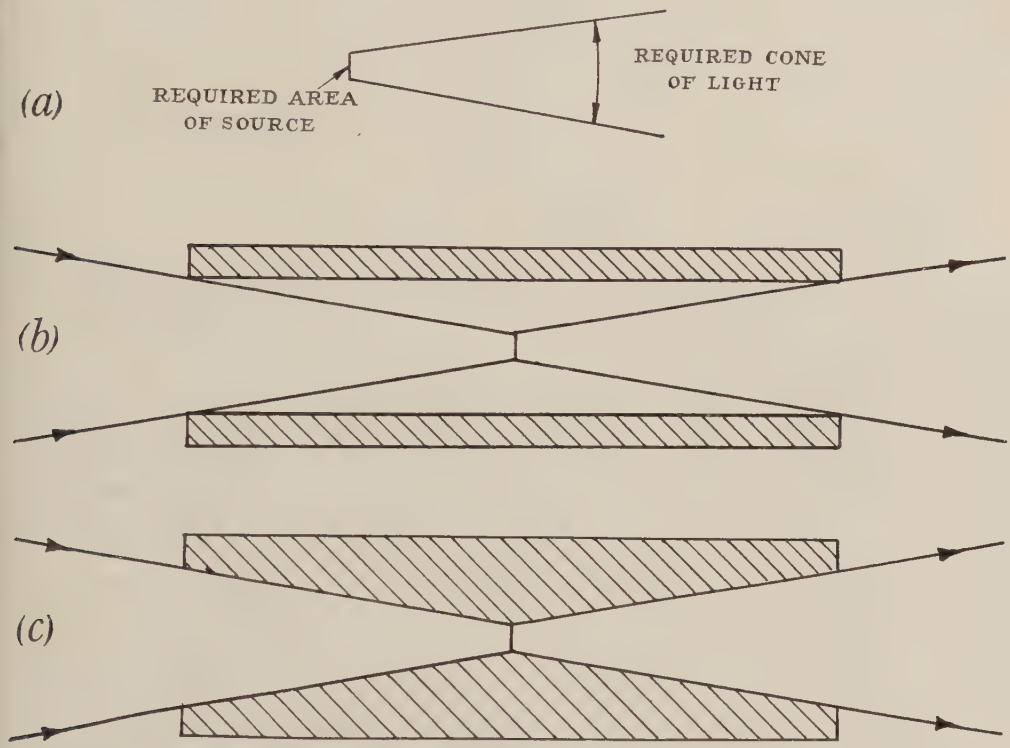


Fig. 6. (*a*) Explanatory diagram. (*b*) Parallel-plate Kerr cell. (*c*) Shaped-plate Kerr cell.

The total retardation, ϕ_n, of the new type of cell is readily calculated by means of a simple integration. With reference to figure 7, the retardation produced across the short distance dx is given by

ϕ_n

x

$$d\phi_n = \frac{KE^2 dx}{(d + 2Dx/l)^2},$$

and the total retardation is given by

$$\phi_n = \int_{-\frac{1}{2}l}^{+\frac{1}{2}l} \frac{l^2 KE^2}{(dl + 2Dx)^2}\, dx,$$

which becomes

$$\phi_n = (KlE^2)/dD \qquad \text{.....(6),}$$

where d is the separation at the mid-point of the plates and D the separation at each end. If this is compared with the formula for the retardation for parallel plates

d, D

$$\phi = (KlE^2)/D^2$$

at the separation D that would be necessary to provide the same cone of light and area of source, the gain is immediately apparent. In the cells used at The Gramophone Company's Laboratories, $D/d = 4$ approximately, so that only one-half of the biasing and modulating voltages were necessary compared to those required if parallel plates had been used.

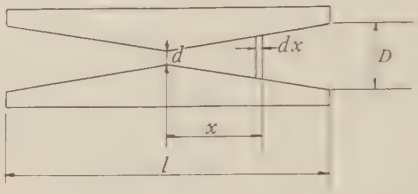


Fig. 7. Dimensions of shaped Kerr-cell plates.

The optimum form of Kerr cell cannot be finally determined until the effect of varying the mid-separation d and the inclination $(D - d)/l$ is known. To produce a given size of spot with a given converging cone of light, a considerable range exists in the choice of the optical system. For instance, a microscope objective might be used, in which case a very small spot and a big cone of light would be required; or were a projection lens used, a much larger source and smaller cone would be necessary to produce the equivalent result on the screen. In practice, so far as television images are concerned, other considerations enter to restrict the choice somewhat, but even so there exists a certain amount of freedom. It then remains to find which combination of Kerr cell and lens is the most efficient in producing a given retardation with the smallest biasing potential.

The practical problem usually presents itself in the form that a certain size of picture is required with a given number of lines using a mirror wheel that has been designed with a reasonable number of mirrors and is of reasonable dimensions; reasonable, that is, with regard to cost and ease of manufacture and adjustment. The size of picture and number of lines determines the size of spot required, the size of picture and number of mirrors determines the distance of the mirror wheel from the screen and the size of mirror wheel determines the aperture of the projection lens and thence the maximum cone of light that could be employed. The remaining unknown is the focal length of the projection lens in order to give the most efficient Kerr-cell operation.

A well-known property of any optical system is the fact that the product of the image height, the sine of the convergent angle of the cone of light and the refractive index is a constant for all the conjugate foci in the system. As the size of spot on the screen and the final convergent cone are fixed, their product will be constant and the same rule will apply at other focussed points in the system, in particular at the Kerr cell which is in a conjugate plane to the screen. Accordingly, if full use is to be made of the projection lens and mirror wheel, the cell must be designed so that

$$d\,(D - d)\,N\,l = Q \qquad (7),$$

where Q is the invariant referred to above, d of course corresponds to the image height, $(D - d)/l$ to the cone of light, and N is the refractive index of the nitrobenzene. Then, from (6) and (7) Q

$$\phi_n = K_2 \frac{D-d}{D} E^2$$

$$= K_2 (1 - d/D) E^2,$$

K_2 being a constant.

To make ϕ_n as great as possible for a given value of E, the ratio d/D should be as small as possible. The difference between ϕ_n when $d/D = \frac{1}{4}$, and in the theoretically best case when $d/D = 0$, is quite small. When $d/D = \frac{1}{4}$,

$$\phi_n = \tfrac{3}{4} \cdot K_2 \cdot E^2;$$

and when $d/D = 0$,

$$\phi_n = K_2 \cdot E^2.$$

The difference amounts, in practice, to only 15 per cent. reduction in the biasing potential. It can therefore be safely concluded that there is little to be gained by reducing d/D below $\frac{1}{4}$. For determining the actual values of d and D, equation (7) shows that as d and D are diminished l also is reduced. The shorter l can be made, the smaller is the loss of light due to absorption in the nitrobenzene. It might possibly have been advantageous to have reduced d below the value of 0·02 in. that was used. The entire absence of sparking and other troubles, however, was very adequate compensation. With the relative values of d, D and l determined on theoretical grounds and the absolute values on practical grounds, it is then an elementary problem in optics to determine the focal length of projection lens required, use being made, of course, of the quantities—aperture, image-distance and so on—that are already known.

§ 6. FREQUENCY RESPONSE

In the introduction it was pointed out that the two main requirements for a light-modulating source were a good frequency-response and high light-efficiency. The design of a Kerr cell for maximum light-efficiency has been dealt with in considerable detail, but nothing has been said with reference to the frequency-response. The reason for this is that little can be done to improve it or make it worse. So far as is known, the Kerr effect in itself will respond to very high frequencies indeed. The limiting factor occurs in applying the high frequencies to a given Kerr cell owing to the capacity of the cell. This consideration will therefore affect the design of the cell to the extent of making it desirable to keep the area of the plates as small as possible and to increase the separation if necessary. Actually, with pure nitrobenzene, little attenuation need be anticipated until frequencies above, roughly, 15,000 ~ have to be dealt with. It may then become necessary to compromise between light-efficiency and frequency-response. In any case the

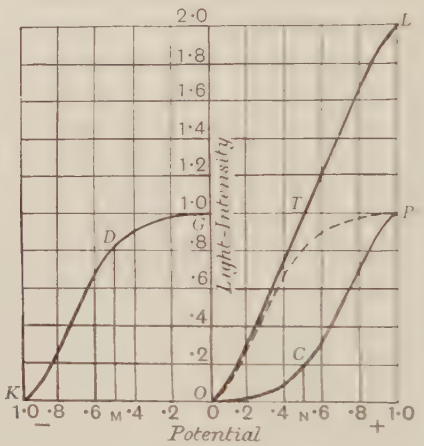
mechanical design of the cell should be such that the areas of the plates are the minimum required for theoretical reasons; the mounting of the plates, for instance, should not involve any increase in their area.

§ 7. ACKNOWLEDGMENT

In conclusion I would like to express to The Gramophone Co. Ltd. my thanks for permission to publish these results, which were obtained in their laboratories.

DISCUSSION

Mr A. J. Maddock. As the potential applied to a Kerr cell is increased, the successive maxima of intensity occur at correspondingly decreased separation. It



OCP, characteristic curve for cell *A*.
KDG, „ „ „ *B* (with optical bias of ¼λ).
OTL, resultant curve for combined effect of two cells.

seems possible, therefore, that at sufficiently high potentials only a narrow spectral region of, say, the blue will be at a minimum with a resultant white colour—an effect somewhat analogous to a thin film of oil on water appearing white when of sufficient thickness. In this way it would appear that for white light at high potentials on the cell the Kerr effect has apparently disappeared though still existing for the various spectral regions. I should like to ask the author if he has experienced this.

As a method of obtaining a linear relation between potential and emergent light-intensity and maximum variation of this latter the following scheme has occurred to me. The light after polarization by the first nicol is divided into two separate beams each passing through a separate Kerr cell and being recombined before traversing the analysing nicol. Corresponding plates of the two cells are connected

in parallel and to the source of modulating potential. Means are arranged for biasing each cell to half the maximum potential and in such a sense that corresponding plates of the two cells are of opposite polarity; thus if the top and bottom plates are correspondingly connected together and to the modulating source, then in cell A the top plate will be made positive with respect to the bottom plate and in cell B the top plate will be negative with respect to the bottom plate. One cell, B, has an optical bias of $\frac{1}{2}\lambda$ as described by the author. Cell A will thus have the characteristic curve OCP in the accompanying figure biased to the point C, whilst cell B will have the curve KDG biased to point D; the intensity of the final emergent beam being given by the sum of the ordinates DM and CN, i.e. point T. As the modulating voltage swings on the positive half-cycle, curves CP and DG are traced out for the two cells, whilst during the negative half-cycle we obtain CO and DK. The intensity of the final beam is the sum of the ordinates of these two curves and is shown at OTL (the dotted curve OP being the curve KDG translated for easy addition of the ordinates). It will be seen that this is sensibly linear over the whole of the range of modulating potential and that the light intensity varies from zero to the full intensity of the initial plane-polarized beam, except for losses in the optical system.

Author's reply. Dr Maddock's anticipation that a point can be reached at which no change in intensity occurs is theoretically quite correct. But it would be difficult to observe such an effect in practice, and personally I have never done so, owing to the very high potential required to produce the phenomenon. An exactly analogous result, however, is produced in photo-elastic experiments and I have discussed this particular point recently*.

The scheme suggested to obtain a more linear relation between potential and intensity is ingenious, and provided it could be successfully put into practice should achieve the desired result. The diagram, however, is somewhat misleading as the apparent advantage of the curve OTL over KDG is to some extent due to the fact that it is drawn on twice the scale. It would be better shown lying between OCP and the dotted curve and drawn as an average rather than as the sum of these two. It is evident that the new curve in that case would be less steep at the lower end than KDG, although over the whole range from O to P the result would certainly be a closer approximation to a straight line.

* R. V. Band and W. D. Wright, "The Analysis of the Colors observed in Photo-elastic Experiments," *J. Opt. Soc. Am.* **20**, 381 (1930).

ON THE FORCES ACTING ON DROPS IN AN ELECTRIC FIELD

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Received January 8, 1932. *Read and discussed February* 19, 1932

ABSTRACT. If whilst a drop of electrolyte is falling in distilled water, a horizontal electric field be established, the drop rapidly spreads out into a filament parallel to the lines of force. An explanation of this phenomenon is given on the basis of the charge at the boundary between conductors that necessarily accompanies the transport of electricity. Experiments with dielectrics and with drops that contract instead of expand are described, and the paper is illustrated with photographs.

§ 1. INTRODUCTION

If two metal plates are immersed in distilled water and a small drop of some coloured electrolyte, such as a solution of potassium permanganate, is allowed to fall between them, then the moment an electric field is established across the plates, the drop begins to spread out laterally into a long filament parallel to the lines of force. With 200 volts across the plates, and with a slowly falling drop, the experiment is very striking and the rate of lateral spreading may easily exceed that of vertical fall under gravity. Experiments can be extended without difficulty to colourless electrolytes by making use of the differences of their refractive indices from that of water. A point source of light casts an easily observable shadow of such a drop, and when the plates are connected to the supply mains the drop is seen to spread out in a similar way.

The classical experiments of Quincke on liquid dielectrics* and the recent experiments of Macky† on the breaking of water globules in strong electric fields deal with related subjects, but the author has so far been unable to find any direct references to the present phenomenon, and as it is possibly new the following investigation has been undertaken.

§ 2. EXPERIMENTAL ARRANGEMENTS

As has already been mentioned the phenomenon may be observed with the very simplest apparatus, but as all is over in a second or two it is desirable to make permanent records which may be examined at leisure. With this in view recourse was had to the shadow cast on a photographic plate by the condensed spark discharge from the secondary of an induction coil. The primary was actuated by contacts carried on the back of the plate carrier, and the plate itself and the carrier were pushed upwards by hand behind a hole of such a size that four ex-

* *Phil. Mag.* **16**, 1 (1883). See also Addenbrooke, *ibid.* **3**, 1116 (1927).
† *Proc. R.S.* **133**, 565 (1931).

Potassium permanganate

Fig. 1. Time, 0 sec.

Fig. 2. Time, 0·6 sec.

Fig. 3. Time, 1·3 sec.

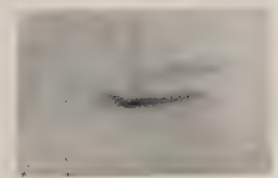

Fig. 4. Time, 1·9 sec.

Sulphuric acid

Fig. 5. Time, 0 sec.

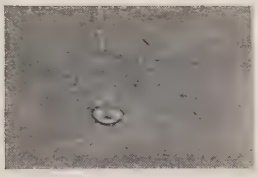

Fig. 6. Time, 0·4 sec.

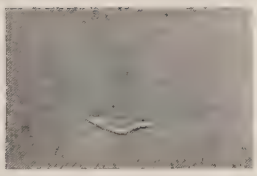

Fig. 7. Time, 1·0 sec.

Fig. 8. Time, 1·3 sec.

Sulphuric acid

Fig. 9. Time, 0 sec.

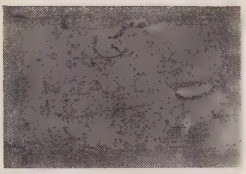

Fig. 10. Time, 0·6 sec.

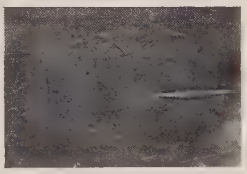

Fig. 11. Time, 1·2 sec.

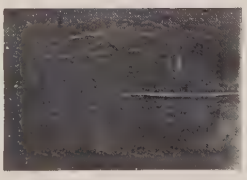

Fig. 12. Time, 1·6 sec.

[*To face p.* 336

Eosin

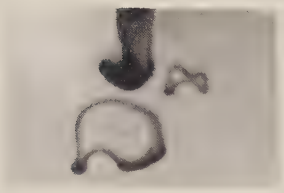

Fig. 13. Time, 0 sec.

Fig. 14. Time, 0·7 sec.

Fig. 15. Time, 1·3 sec.

Fig. 16. Time, 1·8 sec.

Glycerine and water

Fig. 17. Time, 0 sec.

Fig. 18. Time, 0·7 sec.

Fig. 19. Time, 1·7 sec.

Fig. 20. Time, 2·6 sec.

Alcohol and nitrobenzene

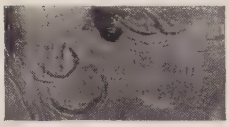

Fig. 21. Time, 0 sec.

Fig. 22. Time, 0·9 sec.

Fig. 23. Time, 1·7 sec.

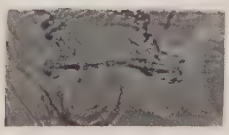

Fig. 24. Time, 2·4 sec.

[*To face p.* 336

posures were possible on one plate. The first two exposures were made without any field, whilst the last two were made with the field switched on. From the first two photographs it was possible to examine any changes taking place in the shape of the drop due to causes other than the electric field, and, from the last two, any changes directly due to this field.

A lens which formed the bob of a short pendulum focussed light from a point source on the side of the plate, and thus provided a time scale of reference. Generally the photographs were taken at intervals of about 0·6 sec.

§ 3. RESULTS

These are embodied in the photographs, figures 1 to 24. Figures 1–12 exhibit drops of initially simple shapes. More often the drops are of complicated shapes, as in figures 13–16. Here the same effect can be traced although it is not at once so obvious. Figures 17–20 represent an effect not yet discussed. Here instead of a drop of electrolyte being allowed to fall into distilled water, a drop of distilled water, whose density had been raised by the admixture of a small quantity of glycerine, was allowed to fall into weak sulphuric acid. The significance of the result will be considered later. In all these cases the difference of potential between the electrodes, which were of platinum, was about 220 V., the positive pole was on the left, and the potential gradient was about 49 V./cm.

Figures 21–24 deal with the case of so-called non-conducting liquids. Here a drop made up of a mixture of nitrobenzene and alcohol was allowed to fall into xylol. The potential difference was much higher and was derived from a small transformer with a step-up ratio of twenty. The r.m.s. voltage on the primary was 65 and the secondary voltage was therefore assumed to be 1300, giving a gradient of 290 V./cm. The significance of this result will likewise be discussed later.

The distilled water used was of the ordinary laboratory type, no special care having been taken with its preparation. Its specific resistance τ varied from τ $1 - 2 \times 10^5$ ohm-cm. and was thus much below the standard of conductivity water.

Data for some solutions used

	Composition of drop	Liquid in which drop falls
Figs. 1–4	0·265 per cent solution potassium permanganate in water $\tau = 635$ ohm-cm.	Water $\tau = 1{\cdot}3 \times 10^5$ ohm-cm.
Figs. 5–12	0·371 per cent solution sulphuric acid in water $\tau = 64$ ohm-cm.	Water $\tau = 2{\cdot}1 \times 10^5$ ohm-cm.
Figs. 13–16	0·37 per cent solution eosin in water $\tau = 1520$ ohm-cm.	Water $\tau = 1{\cdot}0 \times 10^5$ ohm-cm.
Figs. 17–20	0·37 per cent solution glycerine in water $\tau = 1{\cdot}6 \times 10^5$ ohm-cm.	Very weak sulphuric acid $\tau = 1{\cdot}48 \times 10^4$ ohm-cm.
Figs. 21–24	Alcohol 5 parts (Dielectric constant = 27); nitrobenzene (about 1 part) (Dielectric constant = 34)	Xylol (Dielectric constant = 2·4)

§ 4. DISCUSSION OF RESULTS

Although the phenomenon under observation was first noticed with drops of an electrolyte in distilled water, it is theoretically simpler to start with the case of the so-called non-conducting liquids exhibited in figures 21–24. Here a liquid of specific inductive capacity about 28 is dropped into one of specific inductive capacity 2·4. As a result, the lines of force crowd into the globule in the well-known fashion*, and the concentration at the poles of a spherical globule rises to $3K_2/(K_2 + 2K_1)$ times the undisturbed value, where K_2 is the dielectric constant of the globule and K_1 that of the medium into which it is dropped. In the present case, therefore, the concentration is 2·6 times the normal field, whilst for a drop of infinite dielectric constant the concentration would be 3·0 times.

This concentration is a very obvious feature, but, if we wish to explain the sideways spreading of the drop, we must look to the change in tension that occurs when a tube of force passes from one medium to another, even when there is no such concentration. The surfaces of a slab of dielectric, for instance, placed between the flat plates of a condenser, experience forces tending to pull them across to the plates. The tension per cm.² of dielectric surface is easily calculated, for the tension per cm.² outside the slab is $K_1F_1^2\,8\pi$ whilst that within the slab is $K_2F_2^2\,8\pi$, where F_2 and F_1 represent the respective potential gradients within and without the slab. The resultant tension per cm.² towards either plate is therefore

$$K_1F_1^2/8\pi - K_2F_2^2/8\pi \qquad \text{.....(1),}$$

or, using the normal boundary condition, we may write it

$$(K_1F_1^2/8\pi)\,(1 - K_1/K_2) \qquad \text{.....(2).}$$

For a dielectric of infinite specific inductive capacity this would be $K_1F_1^2\,8\pi$, whilst for the dielectrics in this experiment it would be 0·91 of this value.

In the region of the poles of a spherical droplet, therefore, where the tubes of force pass almost normally into the surface, there is a tension not far short of that which would be experienced by a metallic globule of the same size, and it is to this tension that we must attribute the lateral spreading shown in figures 21–24.

The case of an electrolyte is a little more complicated. First of all the drop is in general not quite at the same potential as the solution into which it falls, and thus has a resultant charge. This resultant charge is small, however, and in any case will only cause a drift of the drop to one or other electrode. It will thus in no wise explain the lateral spreading.

As the voltage gradients employed in this work are comparatively large, we shall, as a simplification, use Ohm's Law and deal with our electrolytes as with metallic conductors, writing

$$(1/\tau_1)\,(dv_1/dn) = (1/\tau_2)\,(dv_2/dn) \qquad \text{.....(3),}$$

where τ_1 and τ_2 are the specific resistances of the two media and where dv_1/dn and dv_2/dn represent the respective normal potential gradients.

* J. J. Thomson, *Electricity and Magnetism*, chap. 5.

Since the equation is formally similar to the normal condition at a dielectric boundary

$$K_1 dv_1/dn = K_2 dv_2/dn \qquad \ldots\ldots(4),$$

and since moreover the tangential conditions are also the same, the concentration of flow-lines round a highly conducting sphere will be exactly similar to that of the tubes of force in the electrostatic problem.

On the other hand, we must do more than concern ourselves with formal similarities. In the actual problem electrostatic and electrodynamic conditions must be simultaneously satisfied. Yet as they stand (3) and (4) either imply that K_1/K_2 is equal to τ_1/τ_2 or else are mutually exclusive. The difficulty disappears however if there is a free charge σ per cm^2 of boundary*, for we may then write σ

$$K_1 dv_1/dn - K_2 dv_2/dn = 4\pi\sigma \qquad \ldots\ldots(5),$$

and it is now possible for (3) and (4) to be simultaneously true. Thus when we consider a droplet of comparatively high conductivity placed in a medium of low conductivity, we have not only to consider the bound charges at the surface resulting from the polarized ends of the molecules, but also the superposed free charges. Although therefore equation (1) is still true, (2) is not, and we must now substitute from (3) instead of from (4). Thus we have

$$\text{Resultant tension per cm}^2 = \left(\frac{dv_1}{dn}\right)^2 \left(K_1 - \frac{K_2 \tau_2^2}{\tau_1^2}\right) \Big/ 8\pi \qquad \ldots\ldots(6).$$

It might at first be thought that this expression should tend towards (2) as the specific resistances became very great. It will be observed, however, that it does not. The truth is that the electrostatic condition (4) and the electrodynamic condition (3) represent respectively the far removed initial and the steady conditions. In the case of a very poor conductor, the attainment of the latter would take a considerable time and the free surface charge would only slowly develop, whereas, in the case of a comparatively good conductor such as an electrolyte, the steady condition would be attained in the merest fraction of a second. Actually, in the case of the nitrobenzene-and-alcohol droplet in xylol, it is probable† that quite a considerable amount of free surface charge would be developed even in 0·01 sec. Strictly, therefore, in this case the phenomenon should be regarded as intermediate between the two extremes. Keeping all this in mind, let us now proceed to make a comparison between the rates of vertical fall and lateral spreading of a drop. Let us first consider a central vertical column of radius r that runs through a drop r of radius R. The resultant gravitational pull downwards is given by R

$$\pi r^2 . 2R (\rho_2 - \rho_1) g,$$

where $(\rho_2 - \rho_1)$ is the difference of the densities of the drop and the water, and ρ_2, ρ_1 where g is the acceleration of gravity. Hence the resultant pressure at the bottom g

* J. J. Thomson, *Electricity and Magnetism*, chap. 9; or J. H. Jeans, *Electricity and Magnetism*, chap. 10.

† The time relaxation is given by $\exp(-4\pi t/\kappa\tau)$; see J. H. Jeans, *Electricity and Magnetism*, chap. 10.

of the drop is $2R(\rho_2 - \rho_1)g$. In the case of the drop of potassium-permanganate solution, $(\rho_2 - \rho_1) = 0{\cdot}0017$ gm./cm. and $R = 0{\cdot}15$ cm. roughly. Hence the resultant pressure at the lowest point is approximately 0·5 dyne cm.^{2}

To obtain the lateral pull, we must revert to (1) and estimate the values of the potential gradients within and without the drop in the region of a pole. We know that within the drop*

$$\frac{dv_2}{dn} = \left(\frac{3dv}{dn}\right) \Big/ \left(\frac{\tau_1}{\tau_2} + 2\right),$$

where dv/dn is the potential gradient in a region remote from the drop. Now in the case of the drop under consideration $\tau_1/\tau_2 = 1{\cdot}3 \times 10^5/635$ and hence

$$dv_2/dn = 0{\cdot}014\ dv/dn.$$

Outside the drop dv_1/dn has τ_1/τ_2 times this value or nearly $3dv/dn$. Hence the resultant tension per cm.^{2} may be written

$$\left\{K_1\left(\frac{3dv}{dn}\right)^2 - K_2\left(\frac{0{\cdot}014dv}{dn}\right)^2\right\} \Big/ 8\pi.$$

Now K_1 the dielectric constant of water is 80, and that of an electrolyte is of the same order†, hence the tension per cm.^{2} may be written $28{\cdot}6\ (dv/dn)^2$. The potential gradient used, namely 49 V./cm.‡, corresponds to 0·16 e.s.u. cm. and hence the tension per cm.^{2} works out to 0·7 dyne. It thus appears that, in the case of the permanganate droplet, the lateral and vertical forces per cm.^{2} are of the same order, being respectively 0·7 and 0·5 dyne. Unless therefore the droplet offers any appreciable resistance to deformation of shape§, we should expect the initial lateral movement not to be very different from the rate of fall.

An inspection of the photographs shows that the lateral spreading is rather faster than has been indicated, but there is no difficulty in accounting for this. We have considered only a spherical drop. The concentration of lines of force at the poles of a spheroidal drop, with its long axis parallel to the field, is very much greater, and there is thus a correspondingly increased tension on the ends.

There is one further matter that needs consideration. The elongated droplet referred to, carries a much denser current than the liquid around. Now the cross section of the drop can be split into a number of current-carrying filaments, and each of these filaments attracts its neighbours, so that there is thus a tendency for the drop to reduce its diameter. An estimate of the order of the pressure tending to cause this reduction can be obtained from the expression for the lateral pressure of the magnetic tubes of force, but a more exact calculation is not difficult, and, for a long cylinder, the pressure works out to be the square of the current divided by the cross-section. As the current is a mere fraction of an ampère the pressure is quite negligible, and we need not concern ourselves any more with this factor.

* J. J. Thomson, *Electricity and Magnetism*, chap. 5.

† R. T. Lattey and W. G. Davies, *Phil. Mag.* **12**, 1111 (1931).

‡ It will be noted that, owing to the high dielectric constant of water, this value is much less than in the case of xylol.

§ It would be necessary to take account of this resistance if there were an appreciable interfacial surface tension, or if the internal and external lateral pressures of the tubes of force around an equatorial band were seriously different.

So far then our explanations appear to be satisfactory, but one obvious confirmatory experiment remains to be performed, namely, the production of a lateral contraction instead of a lateral spreading. For this to happen, it is clear that we must make the tension inside the drop greater than that outside. In other words, the drop must be of low conductivity and the surrounding liquid of comparatively high conductivity. With this in view, therefore, a mixture of glycerine and water of specific resistance $1{\cdot}6 \times 10^5$ ohm-cm. was dropped into weak sulphuric acid of specific resistance $1{\cdot}5 \times 10^4$ ohm-cm. Here dv_2/dn works out to be $1{\cdot}4\, dv/dn$, whilst dv_1/dn is approximately one-tenth of this value. Hence since K_1 and K_2 are not very different, the resultant contracting tension may be written

$$80\left\{\left(\frac{0{\cdot}14\,dv}{dn}\right)^2-\left(\frac{1{\cdot}4\,dv}{dn}\right)^2\right\}\Big/8\pi,$$

which $= -0{\cdot}16$ dyne/cm^2. This is approximately one-quarter the previous expanding tension, but an inspection of figures 17–20 leaves no doubt about its existence, and the theory is thus confirmed.

It appears possible, therefore, to give a satisfactory explanation of the lateral spreading of drops of one electrolyte in another on the basis of the change of tension in the tubes of force as they pass a surface of separation. We can further regard this change of tension as arising, in dielectrics, from a polarization charge at the surface, and, in conductors, from a combination of free and polarization charges.

DISCUSSION

Mr R. H. Humphry (communicated). The experiments which Dr West has carried out have an important bearing on the observation of cataphoresis in colloidal solutions. In the usual method of making such observations the motion of a surface of separation in an electric field is observed, and if there is a difference between the conductivities or between the dielectric constants of the solution and the dispersion medium, as is generally the case, effects such as those mentioned in this paper are likely to vitiate the results of such measurements. Experiments not unlike those of Dr West were carried out some time ago in the course of an investigation of cataphoresis in non-aqueous media*. In subsequent experiments by Dr R. S. Jane and myself†, in which we used the Toepler *schlieren* method to render visible a stream of a solution of rubber in benzene flowing in benzene between electrodes, we were careful to arrange that the dielectric constant of the solution was practically the same as that of the dispersion medium, namely 2·2 for rubber and 2·29 for benzene. It was found that careful drying of the substances used completely changed the effect, no spreading of the stream being observed in the case of the dry solution; apparently water, with its high dielectric constant, may, even in very small quantities, play an important part in these "non-aqueous"

* R. H. Humphry, *Koll. Zeit.* **38**, 306 (1926).

† R. H. Humphry and R. S. Jane, *Trans. Faraday Soc.* **22**, 420 (1926); *Koll. Zeit.* **41**, 293 (1927).

solutions. These experiments have been discussed critically by Büchner and van Royen* who also considered the conditions for the spreading (or otherwise) of drops in electric fields.

It would be of interest to know whether any experiments have been carried out with alternating fields. Since the pull is proportional to the square of the electric field, the spreading of the drop should occur equally in an alternating field. On the other hand, if electric charges are present the force on these would be proportional to the first power of the field and an alternating field would have no resultant effect on them. In the experiments referred to on rubber and benzene we found that, while spreading occurred in a direct field, no such effect was observed when an alternating field of the same intensity was used.

Author's reply. Mr Humphry's experiment, in which a cylindrical stream of rubber solution is drawn out into a fan by an electric field, certainly resembles the present experiments with electrolytes, whilst those he mentions of Büchner and van Royen resemble them still more closely. The methods used differ, of course, but, despite this, there is good agreement between the conclusions reached by these workers and by the author.

It is suggested that in Mr Humphry's undried solutions a certain amount of conduction takes place. If, further, the rubber solution were the better conductor, the stream would spread for much the same reason as do the drops of electrolyte in the present work. Careful drying would greatly reduce the effect by reducing the conductivity and thus increasing the time the charges take to form i.e. the "time of relaxation" referred to in the paper.

In reply to Mr Humphry's last query: experiments made with 50 ~ alternating currents showed that the effect still took place. Any charges developed at the ends of a drop change sign with the field in much the same way as would the charges at the ends of a metallic conductor in a similar alternating field. Owing mainly to the higher resistance of the drop, however, the time taken for the charges to reach their full values would be greater, and, with sufficiently high frequencies, the tendency to spread would thus become progressively smaller. Apparently the time the charges take to form in Mr Humphry's high-resistance solutions is considerably greater than the period of the alternating field. In the absence of such charges, therefore, and with equal dielectric constants, there is no reason why the stream should spread. The present work would thus appear to throw some light on Mr Humphry's results.

* E. H. Büchner and A. H. H. van Royen, *Koll. Zeit.* **49**, 249 (1929).

THE FIRST SPARK SPECTRUM OF ARSENIC (As II)

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Communicated by Prof. A. Fowler, F.R.S., February 3, 1932.
Read March 18, 1932

ABSTRACT. The spectrum of arsenic has been examined under varying conditions of excitation, and lines belonging to the singly-ionized atom have been identified. Combinations between the deep terms of the singlet and triplet system of As II have been discovered; about 70 lines have entered into the classification. A provisional term scheme, based on two members of the singlet series $5s\ ^1P - mp\ ^1D$, is set up. The largest term $4p\ ^3P_0$ (ν 162788) leads to an ionization-potential of about 20·1 V.

§ 1. INTRODUCTION

In continuation of the previous work by the writer*, on the second spark spectrum of arsenic, the following paper gives a preliminary account of the regularities that have been obtained in the first spark spectrum of arsenic. It is based on an experimental investigation of the spectrum under different conditions of excitation. The work has been made possible in the first instance by the data, kindly supplied by Prof. R. A. Sawyer, of the spark spectrum of arsenic in the vacuum-grating region down to λ 370 Å. Of the published wave-lengths in this region, those of Queney† also were made use of. When the author, on the basis of the above results, had worked out the preliminary analysis of the spectrum of As II, discussed below, he had an opportunity of looking into the unpublished results obtained independently by K. R. Rao, with which there is found to be a very good agreement in the main features of the scheme. It is therefore considered desirable to publish this preliminary account pending a more detailed study of the spectrum, which is in progress.

§ 2. EXPERIMENTAL

The spark spectrum of arsenic was studied in the visible and the quartz regions by a 10-ft. concave grating in an Eagle mounting and a Hilger E_2 quartz spectrograph. The spark was produced between electrodes of pure arsenic in air and in hydrogen at varying pressures, by a $\frac{1}{2}$-kilowatt 20,000-volt transformer. To distinguish lines due to different stages of ionization, the spectrum was photographed under varying degrees of discharge; to this end a variable self-inductance and capacity were included in the secondary circuit. An auxiliary spark-gap in air was also placed in series with the experimental spark-gap. Discharge through the vapour

* *Ind. J. Physics*, **3**, 437 (1929).
† *J. de Phys. et la Rad.* **10**, 448 (1929).

of pure metallic arsenic and arsenic trichloride was also studied, the length of the spark-gap being varied. The lines of the tube discharge were very sharp. The chlorine lines visible on the plates were first identified and eliminated. For measuring the wave-lengths in these regions the lines of the iron arc were used as standards. The already-published analyses of As I, As III, and As IV also have helped in the identification of lines belonging to the spectrum of singly-ionized arsenic.

§ 3. RESULTS

The terms which are to be expected in the spectrum of As II according to Hund's theory are given below in table 1.

Table 1. Predicted terms of As II.

1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	Term prefix	Terms
2	2	6	2	6	10	2	2	.	.	.	.	.	$4p$	$^3P\ ^1D\ ^1S$
2	2	6	2	6	10	2	1	.	.	1	.	.	$5s$	$^3P\ ^1P$
2	2	6	2	6	10	2	1	1	.	.	.	.	$4d$	$^3F\ ^3D\ ^3P\ ^1F\ ^1D\ ^1P$
2	2	6	2	6	10	2	1	.	.	.	1	.	$5p$	$^3D\ ^3P\ ^3S\ ^1D\ ^1P\ ^1S$
2	2	6	2	6	10	2	1	.	1	.	.	.	$4f$	$^3G\ ^3F\ ^3D\ ^1G\ ^1F\ ^1D$

It is evident from the table of predicted terms of As II that the strongest lines in the spectrum should correspond to the transitions $4p - 5s$ and $4d$. The location of the triplet $4p\ ^3P - 5s\ ^3P$ formed the starting point of the classification. The position of this triplet in the analogous spectra of other elements is represented below.

	$mp\ ^3P_2 - (m+1)s\ ^3P_2$		
C I	60350	N II	148943
Si I	39732	P II	86656
Ge I	37708	As II	(78967)
Sn I	35201	Sb II	—

It is expected from such a comparison that in As II this group may occur in the region ν 80000, which is found to be also a region in which some of the strongest unclassified lines of the arsenic spark spectrum occur. Further, the elimination from the lines in this region of a few belonging to As IV and As III* at once led to the identification of the combination $4p\ ^3P - 5s\ ^3P$, represented in table 2. It is gratifying to note that in one of the plates taken by K. R. Rao, at Upsala, of the vacuum spark spectrum with a certain amount of inductance in series, this group stands out clearly isolated in the appropriate region. About 5000 cm.$^{-1}$ from this group and towards the region of larger wave-length, where the strong singlet $4p\ ^1D_2 - 5s\ ^1P_1$ might be expected, there are two intense lines λ1375 and 1369. Of these the former has proved to be the required line, supported by the presence of all the intercombination lines. The level $4p\ ^1S_0$ has been suggested to the writer by K. R. Rao.

* Rao and Badami, *Proc. R.S.* A, **131**, 154 (1931); K. R. Rao, *Proc. Phys. Soc.* **43**, 68 (1931).

The intervals between the terms of the deepest $4p$ levels being now known, the extension of the regularities further into the violet was considerably facilitated. The relative intensities among the lines constituting any level have led to the probable assignment of the level, which is indicated in table 2.

Table 2. Combinations in As II.

Terms		$4p\ ^3P_0$ 162788		$4p\ ^3P_1$ 161725		$4p\ ^3P_2$ 160248		$4p\ ^1D_2$ 152693		$4p\ ^1S_0$ 140189	
			1063		*1477*		*7555*		*12504*		
$5s\ ^3P_0$	84059	—		77666	(9)	—		—		—	
	397										
$^3P_1$	83662	79128	(10)	78063	(8)	76586	(10)	69030	(3)	56527	(2)
	2381										
$^3P_2$	81281	—		80445	(8)	78967	(10)	71412	(4)	—	
$5s\ ^1P_1$	79972	82816	(5)	81753	(2)	80278	(1)	72724	(10)	60219	(8)
$4d\ ^3D_1$	63723	99065	(8)	98002	(6)	—		88964	(2)	76470	(4)
	483										
$^3D_2$	63240	—		98485	(10)	97008	(2)	—		—	
	842										
$^3D_3$	62398	—		—		97851	(10)	90294	(6)	—	
$4d\ ^1D_2$	60305	—		—		99944	(3)	92387	(10)	—	
$4d\ ^1P_1$	61302	101485	(4)	100423	(3)	98945	(2)	91391	(6)	78889	(10)
$4d\ ^1F_3$	52916	—		—		107335	(1)	99774	(8)	—	
α	79688	—		—		80561	(3)	73004	(5)	—	
β	78156	84634	(3)	83570	(1)	82092	(1)	74537	(1)	62030	(1)
γ	73962	—		87765	(2)	86285	(2)	—		—	
δ	73240	—		—		87007	(4)	79453	(2)	—	
ϵ	60193	—		101531	(5)	100054	(3)	92501	(4)	79996	(1)

Terms		$5p\ ^3S_1$ 61702	$5p\ ^1D_2$ 60399	$5p\ ^1P_1$ 63610	$5p\ ^1S_0$ 58735
$5s\ ^3P_0$	84059	22358·1 (5)	—	20449·4 (8)	—
	397				
$^3P_1$	83662	21960·4 (7)	23263·1 (6)	20052·1 (9)	24926·5 (5)
	2381				
$^3P_2$	81281	19580·5 (8)	20882·9 (6)	17671·6 (8)	—
$5s\ ^1P_1$	79972	18270·0 (6)	19572·4 (8)	16360·3 (10)	21235·5 (7)

The group $4d\ ^3D$ has been tentatively suggested. The alternative group shown in table 3 has been identified by K. R. Rao.

Table 3.

	$4p\ ^3P_0$	$^3P_1$	$^3P_2$
$4d\ ^3D_1$	99065 (8)	98002 (6)	—
149			
$^3D_2$	—	97851 (10)	96373 (4)
2111			
$^3D_3$	—	—	98485 (10)

The partial inversion of the term $4d\,^3D$ is, of course, then in keeping with the corresponding feature in Ge I. But the line ν 96373 is not found in the list used by the writer; the first group is therefore retained. Until the analysis has been extended so as to identify the combinations of the $4d$ term with the $5p$, or more probably with the $4f$ terms, the allocation of the various other energy levels in table 2 is difficult; so only arbitrary symbols have been used to designate these levels. Besides those which are given in this table many more could be found by searching through the list of recurring frequency-differences. They have, however, been omitted.

The spark spectrum of arsenic is exceedingly rich in lines, in the visible and the quartz regions, which have to be assigned to the singly-ionized atom of the element. Our knowledge of the intervals of the $5s\,^3P$ term affords a clue to the extension of the analysis of the spectrum into this region. A search for lines giving the differences 2381 cm.$^{-1}$ and 397 cm.$^{-1}$ (equal to $5s\,^3P_1 - 5s\,^3P_2$ and $5s\,^3P_0 - 5s\,^3P_1$) did not lead to the location of any satisfactory group which could be ascribed to the combination $5s\,^3P - 5p\,^3P$. It is believed that this group, as also the group $5s\,^3P - 5p\,^3D$, lies partially in the red region, which has not yet been quite satisfactorily investigated. Experiments with a view to identifying these are in progress. Some of the singlets, supported by intercombinations, have been discovered and have led to a preliminary evaluation of the characteristic terms. It is evident from an examination of these that the strong and diffuse groups of lines in the visible region referred to above are probably due to the transition of the series electron $4d \rightarrow 4f$, which gives rise to several multiplets of the type $^3D^3F$, $^3D^3D$, $^3P^3D$, etc. Further attempts at analysis are being made on the lines of this suggestion.

There are three strong pairs with wave-number difference 720 cm.$^{-1}$, which within limits of experimental error is equal to the difference between the levels $(\gamma - \delta)$. Hence the classification of these pairs shown in table 4 is adopted. The terms a, b, c may belong to the configuration $4f$. A few other combinations between these and other known levels are also given below.

Table 4. (Cf. table 2.)

Terms		*a* 41268	*b* 43887	*c* 41318
γ	73962	32690·6 (6)	35309·6 (6)	32739·9 (6)
δ	73240	31970·4 (6)	34589·1 (3)	32019·7 (4)
$4d\,^3D_1$	63723	—	25072·9 (1)	—
	483			
$^3D_2$	63240	21975·7 (7)	—	—
	842			
$^3D_3$	62398	21131·7 (8)	—	—
$^1D_2$	60305	19033·7 (5)	21651·8 (6)	19083·5 (4)

The differences 397 and 2381 occur also in the pairs, given in table 5, which might form part of the transition $5s \rightarrow 5p$.

Table 5.

λ	Int.	ν	δν
5620·86	10	17786·0	
5498·01	7	18183·4	397·4
6405·95	4	15606·2	
5558·34	8	17986·0	2379·8
5331·47	7	18751·4	
4730·90	8	21131·7	2380·3

§4. TERM VALUES

A provisional estimate of the term values is made possible by the detection of two members of the singlet series $5s\ ^1P_1 - mp\ ^1D_2$.

$$5s\ ^1P_1 - 4p\ ^1D_2 = -\ 72724$$
$$5s\ ^1P_1 - 5p\ ^1D_2 = \quad 19572$$
$$\text{Limit} \quad 5s\ ^1P_1 = \quad 79972.$$

This value is adopted for $5s\ ^1P_1$ in the following list of characteristic term values in the spectrum of As II.

Table 6. Term values of As II.

$4p\ ^3P_0$	162788	$^3P_2$	81281	$5p\ ^1P_1$	63610	ϵ	60193
$^3P_1$	161725	$^1P_1$	79972	$4d\ ^3D_2$	63240	$5p\ ^1S_0$	58735
$^3P_2$	160248	α	79688	$4d\ ^3D_3$	62398	$4d\ ^1F_3$	52916
$^1D_2$	152693	β	78156	$5p\ ^3S_1$	61702	b	43887
$^1S_0$	140189	γ	73962	$4d\ ^1P_1$	61302	c	41318
$5s\ ^3P_0$	84059	δ	73240	$5p\ ^1D_2$	60399	a	41268
$5s\ ^3P_1$	83662	$4d\ ^3D_1$	63723	$4d\ ^1D_2$	60305		

The comparison in table 7 between the fundamental multiplets in the spectra of Ge I, As II and Se III* is interesting. The wave-numbers given in this table have been reduced for purposes of comparison, according to the method of Millikan and Bowen†.

Table 7.

		$4p\ ^3P_0$	δν	$^3P_1$	δν	$^3P_2$	δν	$^1D_2$	δν
$5s\ ^3P_0$	Ge I			34426					
	As II			67794	33368				
	Se III			102320	34526				
$^3P_1$	Ge I	35234		34677		33824			
	As II	69256	34022	68191	33514	66714	32890		
	Se III	104568	35312	102829	34638	100632	33918		
$^3P_2$	Ge I			36093		35240			
	As II			70573	34480	69095	33855		
	Se III			106437	35864	104242	35147		
$^1P_1$	Ge I							30427	
	As II							62852	32425
	Se III							96411	33559

* Badami and Rao, *Nature*, **128**, 3229 (1931).

† *Phys. Rev.* **26** (1925).

Finally, a list of all wave-lengths of As II that have been classified in this investigation is given below in table 8.

Table 8. List of classified lines of As II.

λ (intensity)	ν	Classification	λ (intensity)	ν	Classification
6110·66 (10)	16360·3	$5s\ ^1P_1 - 5p\ ^1P_1$	1287·57 (9)	77666	$4p\ ^3P_1 - 5s\ ^3P_0$
5657·23 (8)	17671·6	$5s\ ^3P_2 - 5p\ ^1P_1$	1281·01 (8)	78063	$4p\ ^3P_1 - 5s\ ^3P_1$
5471·95 (6)	18270·0	$5s\ ^1P_1 - 5p\ ^3S_1$	1267·61 (10)	78889	$4p\ ^1S_0 - 4d\ ^1P_1$
5252·37 (5)	19033·7	$4d\ ^1D_2 - a$	1266·36 (10)	78967	$4p\ ^3P_2 - 5s\ ^3P_2$
5238·69 (4)	19083·5	$4d\ ^1D_2 - c$	1263·78 (10)	79128	$4p\ ^3P_0 - 5s\ ^3P_1$
5107·82 (8)	19572·4	$5s\ ^1P_1 - 5p\ ^1D_2$	1258·61 (2)	79453	$4p\ ^1D_2 - \delta$
5105·71 (8)	19580·5	$5s\ ^3P_2 - 5p\ ^3S_1$	1250·07 (1)	79996	$4p\ ^1S_0 - \epsilon$
4985·62 (9)	20052·1	$5s\ ^3P_1 - 5p\ ^1P_1$	1245·67 (1)	80278	$4p\ ^3P_2 - 5s\ ^1P_1$
4888·76 (8)	20449·4	$5s\ ^3P_0 - 5p\ ^1P_1$	1243·09 (8)	80445	$4p\ ^3P_1 - 5s\ ^3P_2$
4787·27 (6)	20882·9	$5s\ ^3P_2 - 5p\ ^1D_2$	1241·29 (3)	80561	$4p\ ^3P_2 - \alpha$
4730·90 (8)	21131·7	$5s\ ^3D_3 - a$	1223·19 (2)	81753	$4p\ ^3P_1 - 5s\ ^1P_1$
4707·79 (7)	21235·5	$5s\ ^1P_1 - 5p\ ^1S_0$	1218·14 (1)	82092	$4p\ ^3P_2 - \beta$
4617·27 (6)	21651·8	$4d\ ^1D_2 - b$	1207·50 (5)	82816	$4p\ ^3P_0 - 5s\ ^1P_1$
4552·37 (7)	21960·4	$5s\ ^3P_1 - 5p\ ^3S_1$	1196·60 (1)	83570	$4p\ ^3P_1 - \beta$
4549·22 (7)	21975·7	$4d\ ^3D_2 - a$	1181·55 (3)	84634	$4p\ ^3P_0 - \beta$
4471·41 (5)	22358·1	$5s\ ^3P_0 - 5p\ ^3S_1$	1158·95 (2)	86285	$4p\ ^3P_2 - \gamma$
4297·45 (6)	23263·1	$5s\ ^3P_1 - 5p\ ^1D_2$	1149·33 (4)	87007	$4p\ ^3P_2 - \delta$
4010·66 (5)	24926·5	$5s\ ^3P_1 - 5p\ ^1S_0$	1139·40 (2)	87765	$4p\ ^3P_1 - \gamma$
3987·24 (1)	25072·9	$4d\ ^3D_1 - b$	1124·05 (2)	88964	$4p\ ^1D_2 - 4d\ ^3D_1$
3126·99 (6)	31970·4	$\delta - a$	1107·49 (6)	90204	$4p\ ^1D_2 - 4d\ ^3D_2$
3122·18 (4)	32019·7	$\delta - c$	1094·20 (6)	91391	$4p\ ^1D_2 - 4d\ ^1P_1$
3058·10 (6)	32690·6	$\gamma - a$	1082·40 (10)	92387	$4p\ ^1D_2 - 4d\ ^1D_2$
3053·49 (6)	32739·9	$\gamma - c$	1081·07 (4)	92501	$4p\ ^1D_2 - \epsilon$
2890·24 (3)	34589·1	$\delta - b$	1030·84 (2)	97008	$4p\ ^3P_2 - 4d\ ^3D_2$
2831·26 (6)	35309·6	$\gamma - b$	1021·96 (10)	97851	$4p\ ^3P_2 - 4d\ ^3D_3$
λ vac.			1020·39 (6)	98002	$4p\ ^3P_1 - 4d\ ^3D_1$
1769·06 (2)	56527	$4p\ ^1S_0 - 5s\ ^3P_1$	1015·38 (10)	98485	$4p\ ^3P_1 - 4d\ ^3D_2$
1660·60 (8)	60219	$4p\ ^1S_0 - 5s\ ^1P_1$	1010·66 (2)	98945	$4p\ ^3P_2 - 4d\ ^1P_1$
1612·11 (3)	62030	$4p\ ^1S_0 - \beta$	1000·44 (8)	99965	$4p\ ^3P_0 - 4d\ ^3D_1$
1448·64 (1)	69030	$4p\ ^1D_2 - 5s\ ^3P_1$	1002·27 (8)	99774	$4p\ ^1D_2 - 4d\ ^1F_3$
1400·32 (4)	71412	$4p\ ^1D_2 - 5s\ ^3P_2$	1000·56 (3)	99944	$4p\ ^3P_2 - 4d\ ^1D_2$
1375·07 (10)	72724	$4p\ ^1D_2 - 5s\ ^1P_1$	999·46 (3)	100054	$4p\ ^3P_2 - \epsilon$
1369·78 (5)	73004	$4p\ ^1D_2 - \alpha$	995·79 (3)	100423	$4p\ ^3P_1 - 4d\ ^1P_1$
1341·53 (1)	74537	$4p\ ^1D_2 - \beta$	985·37 (4)	101485	$4p\ ^3P_0 - 4d\ ^1P_1$
1307·76 (3)	76470	$4p\ ^1S_0 - 4d\ ^3D_1$	984·92 (5)	101531	$4p\ ^3P_1 - \epsilon$
1305·72 (10)	76586	$4p\ ^3P_2 - 5s\ ^3P_1$	931·66 (1)	107335	$4p\ ^3P_2 - 4d\ ^1F_3$

§ 5. ACKNOWLEDGMENTS

In conclusion I wish to express my grateful thanks to Prof. A. Fowler and Dr T. Royds for their interest in the work, and to Dr K. R. Rao for his very helpful suggestions.

THE PHOTOGRAPHIC MEASUREMENT OF THE ABSORPTION COEFFICIENTS OF GAMMA-RAYS FROM RADIUM (B + C)

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Received January 30, 1932. *Read and discussed March* 18, 1932

ABSTRACT. In continuation of earlier work in which the photographic action of γ-rays was examined, the absorption of the γ-rays from radium (B + C) filtered by 1·6 cm. of lead has been measured by a photographic method. With this lead filter the absorption is exponential. The absorption μ_e per electron for the lighter elements is found to be constant, in accordance with the Klein-Nishina formula; and the value, $1{\cdot}56 \times 10^{-25}$, corresponds to a wave-length of 7·0 x.u. The increase of μ_e for the heavier elements in excess of this is found to vary as Z^3, so that the additional absorption is assumed to be due to the photo-electric effect. It has been found that, by assuming the photoelectric term to vary as $\lambda^{2\cdot2}$, an approximate agreement is obtained with the absorption of short X-rays. The intensity of the main γ-rays in the radium (B + C) spectrum after they have passed through 1·6 cm. of lead is calculated by assuming the $\lambda^{2\cdot2}$ law, and it is shown that the intensities are not in contradiction to an effective wave-length of 7·0 x.u. It is shown that the use of limiting channels between the source and absorbers causes scattered, softened γ-rays to be superposed on the main beam.

§ 1. INTRODUCTION

In a previous paper* the photographic action of γ-rays was investigated and the variations of the photographic density produced by γ-rays on photographic film with (i) the time of exposure, and (ii) the intensity of γ-rays, were examined. It was also shown that the photographic method could be used to obtain values of the absorption of γ-rays in lead. If the γ-rays from a constant source, passing through thicknesses d_1 and d_2 of an absorber, took times t_1 and t_2 respectively to produce a certain photographic density, the absorption coefficient μ was shown to be given by

d_1, d_2, t_1, t
μ

$$\mu = (\log t_1 - \log t_2)/(d_1 - d_2).$$

In practice the exact times t_1 and t_2 to produce this particular density need not be known, but if times of exposure were chosen so that densities which did not exceed 0·8 were obtained, the times to produce this given density could be calculated, since, under these conditions, the density was directly proportional to the time of exposure. In any experiment, the object was to produce densities of the same order, as the linear relation between density and time had then to be used only over a small range. The densities used were in the vicinity of 0·6, as the reproducibility of the densities, under the same conditions of exposure, is greatest when the densities are between 0·5 and 0·7.

* J. S. Rogers, *Proc. Phys. Soc.* **43**, 59 (1931).

The relation above has been used to find the absorption coefficients of twenty-two elements. For any element, a series of films were exposed to γ-rays which had passed through different thicknesses of the element. The values of μ were obtained by plotting values of log t against d and measuring the slope of the straight line so produced.

§ 2. PHOTOGRAPHIC TECHNIQUE

Agfa duplitized film was used and was exposed in aluminium film-holders of the type previously described. From a sheet of film 7 in. × 5 in. it was possible to cut 22 pieces of film, and for any one determination the pieces cut from one film were used. After exposure these films were all developed and fixed together, a frame being made so that the pieces could all be clipped in a vertical position, and during development and fixing these were continually agitated in the solutions. A hydroquinone-metol developer was employed, development being for 5 minutes at 18° C. The accuracy of the method depends on the uniformity of the photographic emulsion and generally this was found to be reasonably good. Occasionally a discordant reading in an otherwise concordant set could be accounted for only by an irregularity in the emulsion. In the early stages of the work, the pieces of film for any one determination were not necessarily all selected from the one sheet, but when it was found that pieces from different sheets of film, when exposed and developed together, did not produce densities as uniform as those produced by pieces from the same sheet, all subsequent determinations were made from pieces cut from one sheet. The worst discrepancy from pieces cut from two different films was as follows. The times of exposure to produce a given density from two pieces cut from one sheet were 56 and 55 min. and from four pieces cut from another sheet 61, 63, 63 and 62 min., although the six pieces were all developed together. This variation appears to be exceptional, but it was considered advisable to make the remaining determinations with pieces cut from one film. The films were photometered with a Moll microphotometer, the galvanometer readings being obtained visually.

In all the determinations except some of those with lead and mercury, which were made with the film pressed between aluminium on one side and velvet on the other, lead intensifying-screens were used to shorten the times of exposure. Thin lead foil of mass 0·103 gm./cm.^{2} was pressed against each side of the film. Before the foil was used its intensifying effect was examined. Lead foil was bent and wrapped so that half of the film, back and front, was covered with the lead foil. Figure 1 shows a reproduction of the film together with a graph of the photometered readings. It will be seen that the density-variation from where there was no lead to where the lead was present is quite sharp, indicating that the lateral scattering was small. An apparent gradation in density is due to the heights of the lead foil differing slightly at the back and front of the film. The density produced under the lead foil was approximately twice that where there was no lead, the actual densities

being 0·771 and 0·384. The variation of density with time (constant source), with lead intensifying-screens was found to be a linear one provided the densities did not exceed 0·8.

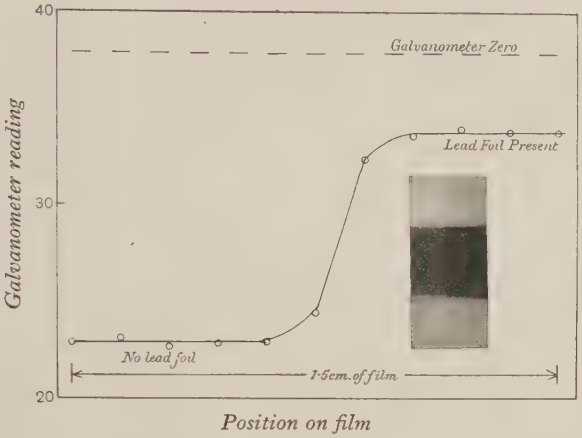

Fig. 1. Effect of lead foil in intensifying the photographic action of γ-rays. Half of the duplitized film was covered on both sides with lead foil of surface-density 0·10 gm./cm^2.

§ 3. EXPERIMENTAL PROCEDURE

A sketch of the apparatus is shown in figure 2. The film is held with its plane vertical in its holder. The rays pass from the source S on to the absorbers A and, after passing through a narrow beam is selected by means of the lead blocks B, 15·3 cm. long, 2·3 cm. wide and 7·5 cm. high so that the rays fall almost normally on the film. An important point to note in the method is that a narrow beam of γ-rays is selected by limiting these *after* they have passed through the absorbers, instead of by the method customarily used in absorption experiments in which the

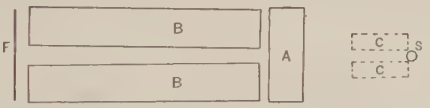

Fig. 2. Sketch of apparatus showing positions of film F, lead blocks B limiting γ-rays falling on film, absorbing screens A, source S, and channel C, C (when used).

beam is limited by a lead channel *before* it reaches the absorbers. The beam selected had a different angular opening when viewed from above from that which it had when viewed from the side. The angular opening from above was 1·2°, but when the beam was viewed from the side, γ-rays at greater angle could affect the film. The distance from the source to film was at least 21·6 cm., but was usually 25 cm. or more. The height of the source when a single tube was used was 4·8 cm. and the height of the film was 0·8 cm. When the distance between these was least, i.e. 21·6 cm., the ray at greatest angle to the horizontal which could pass from source to film was less than 8°, and as cos 8° = 0·990, the departure of the beam from being truly parallel could be neglected. A more likely source of error in the experimental arrangement is that rays could be scattered at greater angles than this

by the absorbers and affect the film. The amount of scattering so produced was small on account of the lateral limitation of the beam and it did not introduce any serious error, as it was found that the values of the absorption coefficients did not depend on the distance of the source to the film. A more conclusive argument is that a determination of the value of μ for copper was made with the solid lead block described below, and the value obtained was 0·391 cm^{-1}. (For this determination, a single glass tube of $RaCl_2$ (100 mg. of Ra) was used in which the volume of the salt was small. The centres of the salt, the lead channel and the film were carefully aligned and the blackening of the exposed portion of the film was found to be uniform.) The γ-rays after they had passed through the absorbers were scattered at the walls of the selecting lead blocks, but this scattering does not affect the accuracy of the results, provided that all beams are similarly treated and that the density on the exposed portion of the film was uniform, as it was found to be.

In measurements of γ-rays with electroscopes and ionization chambers, the natural leak of the vessels must always be found. In the photographic method as used here, what corresponded to the natural leak was being measured while the film was being exposed. To determine the density of any film, the photometer readings through the exposed and unexposed portions were taken. These two readings were obtained on a piece of film 8 mm. wide and 0·24 mm. thick, and the distance between them was 2 cm. or less. The method makes the assumption that the γ-rays scattered by the walls of the room, etc., were of uniform intensity over this portion of film. The natural leak is due to these extraneously scattered rays and in the method the effect of these was being continually recorded on the unexposed portion of the film. In this lies an important advantage of the photographic method, for no ionization vessel could be constructed of as small a volume as that of the film used to determine the density, nor does it seem possible to construct an ionization vessel which will record the main ionization current and the natural leak simultaneously. The experiments were carried out in the strong room of the Commonwealth Radium Laboratory in which there was 1 gm. of radium solution. This was, however, screened by 15 cm. of lead. A glass tube from this solution passed unscreened up one wall of the room and through it to the purifying-apparatus in another room. Several times per week radon was withdrawn from the solution so that there must have been considerable stray γ-radiation in the room. Varying amounts of this was received at different times on the films, as the varying blackening on the unexposed portions of different films showed, but as the same amount was received on the exposed and unexposed portions of any one film, the density due to the γ-rays from the source could still be determined.

The sources used were in glass tubes, each containing approximately 100 mg. of radium, which was in some in the form of the carbonate and in others in the form of the chloride. When no lead filtering was used, a single tube was mounted vertically in a V-shaped slot in the front of a soft wood block. For most of the determinations four tubes contained in brass holders were employed. The holders, 0·8 cm. in diameter, were mounted vertically in holes in a wooden block so that their axes were in line with the central line of the lead channel.

§ 4. MATERIALS USED

When the elements could be obtained in sufficient quantity, a series of rectangular blocks were made, each being carefully machined so as to be of uniform thickness. Their height and width were chosen so that they just covered the ends of the blocks of the lead channel, and hence the addition of a block cut down proportionally the radiation falling on both the exposed and the unexposed portions of the film. For those elements of which only small amounts were obtainable, a tapering rectangular channel was made in a solid lead block 15 cm. long, 7·5 cm. high and 5·5 cm. wide. The dimensions of this channel were 2 cm. × 0·7 cm. at the source end and 2 cm. × 1 cm. at the film end. A single piece of the absorber of known thickness was placed in front of the channel and the absorption of the material was measured relative to lead, a thickness of lead being selected to produce practically the same absorption. The accuracy obtainable with this arrangement, as judged by the reproducibility of the results, was not so great as when a series of blocks could be provided, for with the latter the value of μ was obtained from a straight line drawn through the points from a number of readings. Further, when the channel in the solid block was used, marked variations in the density of the exposed portion of the film were observed, whereas in the other arrangement the density was uniform. This lack of uniformity in the density was due to incorrect alignment of the radium salt within the brass holders with the axis of the lead channel and it makes the results less reliable. The liquids, mercury and bromine, were contained in rectangular glass vessels. Absorption by the glass walls of these vessels was allowed for by obtaining some exposures when the vessels were empty and others when they contained the liquids. A similar glass vessel was used for the uranium, which was in the form of a metal powder rammed tightly into the vessel.

The elements were obtained as pure as possible. The most impure was molybdenum (Kahlbaum) which appeared to be a metal powder compressed with a binding agent. The sample contained a certain amount of air, and when an attempt was made to determine its density by weighing in water, air escaped. The density was found, from a rectangular block, to be 5·20 gm./cm^3, while the true density of molybdenum is 9·0 gm./cm^3. The density of the uranium powder was found by measuring the volume of the powder rammed into a rectangular shape in its glass vessel. Most of the other densities were found by weighing the substances in air and in water, and from the densities the elements appear to be very pure.

The carbon was graphite sheet, which from an analysis by Mr G. Ampt of the Chemistry Department, was 99·75 per cent carbon. The aluminium (British Aluminium Company) was 99·47 per cent pure. The sulphur was cast into rectangular blocks from Merck's "purissimum" crystals, special care being taken that there should be no holes in the blocks. The chromium was prepared by Mr Z. A. Merfield in an arc; the iron was Armco iron; the nickel was 99·53 per cent pure. The copper was cut from a piece of commercial bus bar; a very pure sample of electrolytic copper was discarded on account of tiny holes. The zinc, 99·98 per cent pure, and the cadmium, 99·98 per cent pure, were products of the Electrolytic

Zinc Company of Australia. The bromine and tin were from British Drug Houses, Ltd. The silver, platinum, mercury and bismuth were commercial products. The antimony was "star" antimony, the tungsten was a portion of the anticathode of a Coolidge X-ray tube, the gold was a pure sample which was pressed into uniform thickness. The lead, 99·9915 per cent pure, was from the Broken Hill Associated Smelters, and the uranium powder was from Schering-Kahlbaum*.

§ 5. EXPERIMENTAL RESULTS

A re-examination of the variation of the photographic density with time and with intensity for the γ-rays from radium (B – C) unfiltered except by the glass wall of the containing tube and 3·8 mm. of aluminium film-holder. In the previous paper it was found that with the exception of the γ-rays which were unfiltered, the variations

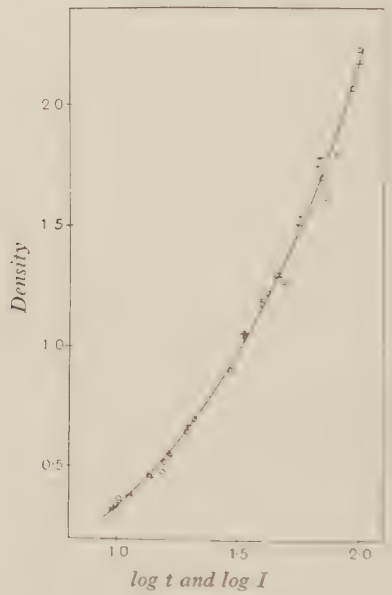

Fig. 3. Filtering of γ-rays by 3·8 mm. of Al + thickness of glass holding radium salt.
○ Points obtained with source of constant intensity, time of exposure being varied.
\+ ,, ,, ,, ,, ,, ,, constant.

of density both with log (time), for a source of constant intensity, and also with log (intensity), for a constant time of exposure, were represented by exactly similar curves. The curves for no-lead-filtering did not coincide, but the readings for these curves were more scattered than for the other curves. As the pieces of film from which the curves were obtained were not selected from the same sheet, it was decided that the readings should be repeated. A larger number of readings than

* The thanks of the writer are due to Mr Ampt for the magnesium, to Mr Merfield for the chromium, to the Defence Department of the Commonwealth of Australia for the nickel, to Prof. Greenwood for the molybdenum and gold, to Prof. Hartung for the bromine and platinum and to the Electrolytic Zinc Company for the zinc and cadmium.

previously were taken for this series, and as far as possible two pieces of film were exposed for each point. Further, the two sets of films, one for the Hurter-Driffield curve (constant intensity) and the other for the characteristic C curve (constant time of exposure) were developed in the same sample of developer, the development of the second set following as quickly as possible after the first. The C curve was obtained from readings spread over a fortnight with a source of originally 100 mc. of radon. The result is shown in figure 3, in which it will be seen that the one curve represents the two sets of readings. The non-agreement of the curves previously published was due, apparently, to experimental errors, and it is to be noted that the earlier curves differed most when the densities exceeded 1·0, in which region the accuracy with the photometer used was least.

Method of obtaining absorption coefficients. In order to illustrate the method and to show the reduction of the results, the readings for a determination of the absorption coefficient of sulphur are given in table 1.

Table 1. Typical set of results.

Element, sulphur. Filtering, 1·6 cm. of lead.

Thickness d of absorber (*cm.*)	Time of exposure (*min.*)	Density D	Time t for $D = 0{\cdot}6$ (*min.*)
6·89	136	0·618	132, 127 } 129·5
	112	0·529	
4·95	105	0·562	113, 108 } 110·5
	111	0·617	
2·61	80	0·547	88, 81 } 84·5
	71	0·617	
1·27	66	0·508	78, 74 } 76·0
	62	0·501	
0	53	0·491	65, 66 } 65·5
	73	0·669	

($\mu = 0{\cdot}097_5$ cm.$^{-1}$ from the straight line obtained when d is plotted against log t.)

The straight line which fits these results is plotted in figure 4, in which the observations for aluminium, cadmium and antimony also are given. It will be seen that the experimental results lie very well on straight lines, so that the value of μ can be obtained from the slope of the straight line drawn through the points. When the readings did not lie so close to the straight line, the method of least squares was employed to calculate μ.

The values of the absorption coefficients of the γ-rays filtered through 1·6 cm. of lead. In the paper already referred to it was shown that the γ-rays from Ra (B + C) were exponentially absorbed in lead when the thickness was not much greater than 1 cm. Throughout these determinations a filter of 1·42 cm. of lead was used, but as the wall of the film-holder was of aluminium 0·38 cm. thick, and as the γ-rays had to pass through the wall of the glass container, the total filtering was equivalent to 1·6 cm. of lead. When the elements could be obtained in block form, sufficient

thicknesses were used to show that d plotted against log t gave a straight line. The results of the determinations are set out in table 2, in the third column of which are the values of μ in cm.$^{-1}$ At least three values were obtained for each element,

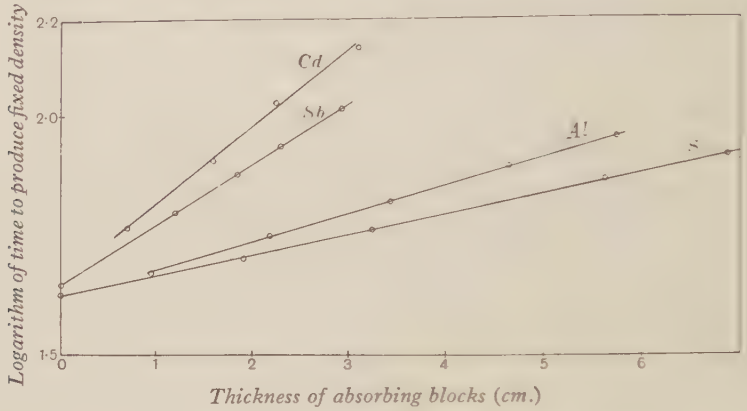

Fig. 4. Absorption curves. Filtering, 1·6 cm. of lead.

Table 2. The absorption coefficients of γ-rays filtered by 1·6 cm. of lead.

Element	Z	μ (cm.$^{-1}$)		ρ (gm./cm.^{3})	$\mu/\rho \times 10^2$	$\mu_e \times 10^{25}$	
		Rogers	Kohlrausch			Obs.	Calc.
C	6	0·080	0·087	1·67	4·79	1·58	1·56
Mg	12	0·081	0·083	1·75	4·63	1·55	1·56
Al	13	0·124	0·126	2·70	4·59	1·57	1·56
S	16	0·094	0·091	1·94	4·84	1·60	1·56
Cr	24	0·293	—	6·96	4·21	1·53	1·57
Fe	26	0·345	0·356	7·87	4·38	1·55	1·57
Ni	27	0·400	0·408	8·99	4·45	1·54	1·57
Cu	29	0·381	0·395	8·91	4·27	1·55	1·57
Zn	30	0·315	0·322	7·14	4·40	1·58	1·58
Br	35	0·126	0·118	3·10	4·42	1·54	1·59
Mo	42	0·230	0·373	5·20	4·42	1·67	1·61
Ag	47	0·462	0·451	10·33	4·46	1·68	1·63
Cd	48	0·372	0·350	8·65	4·46	1·65	1·64
Sn	50	0·293	0·299	7·26	4·04	1·58	1·65
Sb	51	0·291	0·272	6·73	4·32	1·68	1·65
W	74	0·815	0·850	18·81	4·33	1·78	1·84
Pt	78	0·95	—	21·5	4·41	1·83	1·90
Au	79	0·88	0·901	19·26	4·57	1·88	1·91
Hg	80	0·628	0·621	13·6	4·64	1·92	1·92
Pb	82	0·532	0·533	11·37	4·68	1·95	1·95
Bi	83	0·481	0·383	9·81	4·99	2·02	1·96
U	92	0·173	—	3·50	4·94	2·12	2·11

and for those tested in the form of blocks the accuracy, as judged from the mean departure from the mean, was 2 per cent. The accuracy for the other elements was less, about 5 per cent. In the fourth column are given, for comparison, the results of Kohlrausch, taken from page 105 of his book *Probleme der γ-Strahlung*, but the filtering used by him was 4 cm. of lead. It will be seen that except for bismuth,

the agreement between the two sets of results is satisfactory, as Kohlrausch estimated his experimental error to be 5 per cent*. In the fifth column are given the experimentally determined densities ρ, and in the sixth the values of μ/ρ. The mean value of this for the elements investigated is $0{\cdot}045 \pm 0{\cdot}002$, both the light and the heavy elements producing greater values than those in the range $Z = 24$ to 51. In the seventh and eighth columns are given the values of μ_e, the absorption per electron, which is equal to $\mu A/\rho LZ$ where A is the atomic weight, Z the atomic number and L Avogadro's number. In the seventh column are the experimentally determined values of μ_e while the values in the eighth column will be discussed later. The experimental values of μ_e are plotted against Z in figure 5.

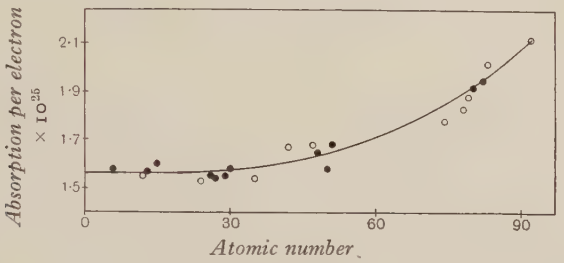

Fig. 5. The variation of the absorption per electron with atomic number. The points shown with filled-in circles are obtained from readings with a series of blocks of the elements.
The full curve is for the equation $\mu_e = 1{\cdot}56 \times 10^{-25} + 7{\cdot}1 \times 10^{-32} Z^3$.

Lead filtering necessary to produce γ-rays from Ra (B + C) which are exponentially absorbed. From table 2 it will be seen that the numerical values of the absorption coefficients agree with those of Kohlrausch, but whereas he found it necessary to filter the rays with 3·5 cm. of lead before they were exponentially absorbed, in these experiments much less lead filtering was required. It would appear that the differences arise from the difference between the experimental arrangements. In the method of Kohlrausch† the source was placed near the centre of an iron sphere 30 cm. in diameter, which was filled with mercury, and a narrow beam of γ-rays passed out through an iron channel before they encountered the absorbers. In the experiments here described, the γ-rays, after being filtered, pass through the absorbing sheets, and then a narrow beam selected by the lead channel can affect the photographic film. It was decided that the conditions of Kohlrausch should be reproduced at least approximately; i.e. the beam was limited before it fell on the absorbers. With the apparatus remaining as before, the source was placed within a lead block and the γ-rays passed out through a narrow channel 6 mm. wide, 3·5 cm. high and 2·5 cm. long. The position of the sides of this channel is shown in figure 2 by C, C. After emergence from this limiting channel the rays fell on the absorbers. The source was in the glass tube alone and the absorption in lead was

* The experimental value of 0·230 cm.$^{-1}$ for molybdenum corresponds to a value of 0·400 cm.$^{-1}$ for the pure metal.

† K. W. F. Kohlrausch, *Wien. Ber.* **126**, 441, 683 and 887 (1917).

measured. The result is shown in figure 6, in which it will be seen that the γ-rays are not exponentially absorbed (with μ equal to 0·523) until they have passed through more than 3 cm. of lead. On the same figure is shown for comparison the absorption of lead when no limiting channel is used. It would thus appear that this limiting channel had a marked effect on the radiation which passed out from it, as a softer radiation was produced. The apparent explanation of this fact is that some of the γ-rays strike the walls of the channel and are scattered into the beam with diminished wave-length (Compton scattering). Thus the relative proportion of the softer radiation present in the beam is increased and a greater thickness of lead is required to filter the beam before it becomes absorbed exponentially. To compare these results further with those of Kohlrausch, the curve shown was

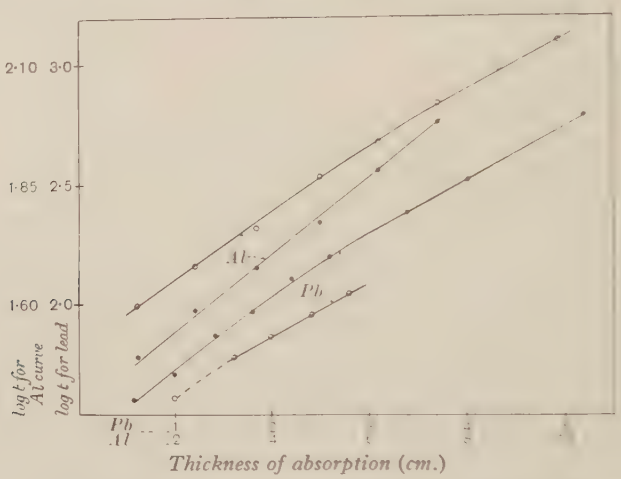

Fig. 6. Graphs of log t/thickness for Al and Pb. The filled-in circles are for readings obtained with lead channel between source and absorbers; the open circles for readings with no lead channel.

analyzed and the absorption coefficient of the softer radiation was calculated. The value found was 1·46 cm.$^{-1}$, while Kohlrausch obtained 1·49; the ratio of the harder to the softer radiation was 4 : 3, again agreeing with his value. The source was then taken out of the lead block and two copper blocks 7·5 cm. + 4·1 cm. were placed in the positions C, C of figure 2. The value of the absorption coefficient of the softer component was then 1·40 cm.$^{-1}$ and the ratio of the harder to the softer radiation was found to be 3 : 2. In the absence of the channel limiting the rays before they encountered the absorbing sheets, there was no evidence of this softer radiation, but a softer radiation with μ equal to 3·0 cm.$^{-1}$ was found. That found by Kohlrausch was 4·6 cm.$^{-1}$

The influence of using the limiting lead channel was also investigated by absorbing the γ-rays in aluminium. The source was placed at the same distance from the film (a) within the lead block and (b) when no such limiting device was used. The results of these two experiments are both shown in figure 6. In the first arrangement the absorption between 1 and 7 cm. was nearly exponential,

with μ equal to 0·178 cm.$^{-1}$, while Kohlrausch found with no lead filter that for the first 6 cm. the value of μ for aluminium was 0·176 cm.$^{-1}$ In the second arrangement, the slope up to 6 cm. was less, and then the absorption was exponential with μ equal to 0·126 cm.$^{-1}$ The absorption coefficient of the softer radiation here present was 0·6 cm.$^{-1}$ as compared with Kohlrausch's 0·57, but no evidence was found of the component with μ equal to 0·229, reported by Kohlrausch. The curves show further that the presence of the lead limiting channel increased the intensity of the γ-rays which fell on the film, and indicated therefore that additional rays were scattered into the beam by it. Thus, when a thickness of 6 mm. of aluminium absorbing sheets was used, in arrangement (*a*) the time to produce a density of 0·6 was 34 min. while with (*b*) the time was 40 min.

§ 6. DISCUSSION OF RESULTS

The relation between the absorption per electron and the atomic number. When a number of different thicknesses of an element were available, the value of μ, from which that of μ_e was calculated, was obtained from a straight line μ which showed that the absorption was exponential. Hence the value of μ had more significance than when a single thickness of absorber was used. The general agreement of the values with those obtained by Kohlrausch has already been mentioned. Although he did not obtain his values of μ by a series of absorbing layers, except for lead, aluminium and tin, he did what was substantially the same thing: he measured the absorption of a single thickness of the absorbing material when the γ-rays were filtered by different thicknesses of lead. He found, from the absorption measurements in lead, that the γ-rays could be analyzed into two components and the relative intensity of the two could be determined. The values of the absorption coefficients of the other elements could then be found. It is the values of μ for the harder component of the γ-rays used by Kohlrausch that agree with those found here. But, as was previously mentioned, the writer has found no evidence of the softer component having μ equal to 1·49 cm.$^{-1}$ in lead in the γ-rays which arise from the source. It was, however, the presence of this softer component in the radiation used by Kohlrausch, that made it necessary to use 3·5 cm. of lead filter before the rays were exponentially absorbed.

When blocks were used, the reading with no absorber present, i.e. for the lead filter alone, was usually omitted, the first reading for the curve being obtained when the lead filter plus a thin thickness of the absorber was present. This arrangement was adopted after it had been found that the reading for the filter alone fell slightly below the straight line representing the points for different thicknesses of the absorber. It was just on this account that the absorption of an element, of which a single thickness only was obtainable, was compared with that of a single thickness of lead which produced nearly the same absorption. In this discussion more weight will be given to the values obtained from straight lines than to the others.

The theory of Klein and Nishina* has been found recently by a number of authors† to account successfully, at least in part, for the absorption of γ-rays. According to this theory, if the absorption is due to scattering alone, the absorption per electron should be independent of the atomic number and be given by

$$\mu_e = \frac{2\pi e^4}{m^2c^4}\left[\frac{1+\alpha}{\alpha^2}\left\{\frac{2(1+\alpha)}{1-2\alpha} - \frac{1}{\alpha}\log(1+2\alpha)\right\} + \frac{1}{2\alpha}\log(1+2\alpha) - \frac{1+3\alpha}{(1-2\alpha)^2}\right],$$

where $\alpha = h\nu/mc^2$. It will be seen, figure 5, that for the lighter elements up to $Z = 35$ μ_e is approximately constant and equal to $1{\cdot}56 \times 10^{-25}$, so that the formula appears valid for the γ-rays from Ra (B + C) filtered by 1·6 cm. of lead for these elements. For the elements of greater atomic number, however, μ_e is greater and increases with the atomic number. A similar increase of μ_e with Z was also found by Ahmad‡, although his values were all higher than those found here. Meitner and Hupfeld§, who measured the absorption in carbon, aluminium and lead of the γ-rays from Ra (B + C) filtered by 4 cm. of lead, found that $\mu_e = 1{\cdot}53 \times 10^{-25}$ for carbon and aluminium and $1{\cdot}996 \times 10^{-25}$ for lead, for which the value here is $1{\cdot}95 \times 10^{-25}$. Tarrant ‖, using 3·2 cm. of lead filter, obtained higher values, viz. $1{\cdot}727$ and $1{\cdot}691 \times 10^{-25}$ for magnesium and aluminium, and $2{\cdot}279$ and $2{\cdot}250 \times 10^{-25}$ for lead and bismuth. In all these determinations the same general result appears, viz. that, while the absorption per electron for the lighter elements is constant, it increases with the atomic number for the heavier ones. The conclusion is therefore, that, while scattering of the type considered by Klein and Nishina accounts for the absorption of the rays from Ra (B + C) in the lighter elements, there must be an additional process for those of greater atomic number. The results here obtained can be accounted for by considering that this additional process is the photoelectric one. The difference between $1{\cdot}56 \times 10^{-25}$ and the values of μ_e for the heavier elements was found to vary as Z^3, and the values of μ_e for all elements can be expressed by the formula:

$$\mu_e = 1{\cdot}56 \times 10^{-25} + 7{\cdot}1 \times 10^{-32} Z^3 \text{¶}.$$

The curve drawn in figure 5 represents this relation, and the eighth column in table 2 is calculated from it. Among elements yielding the more accurate readings, tin shows the greatest departure from the curve, the other elements falling on it within the experimental error. In the X-ray region the atomic absorption coefficient, due to the photoelectric effect, varies approximately as Z^4, and therefore the absorption per electron varies as Z^3. Hence, as the additional absorption for the heavier elements varies as Z^3, it can be assumed that this extra absorption is due to the same process that produces the Z^3 law in the X-ray region—i.e. to the photoelectric effect.

* O. Klein and Nishina, *Z. f. Phys.* **52**, 853 (1928).

† E.g. E. C. Stoner, *Phil. Mag.* **7**, 841 (1929); D. Skobelzyn, *Z. f. Phys.* **65**, 773 (1930); C. Y. Chao, *Phys. Rev.* **36**, 1519 (1930); G. T. P. Tarrant, *Proc. R.S.* **128**, 345 (1930); Lise Meitner and H. H. Hupfeld, *Z. f. Phys.* **67**, 147 (1931).

‡ N. Ahmad, *Proc. R.S.* **104**, 507 (1924). § *Loc. cit.* ‖ *Loc. cit.*

¶ Cf. the equation $\mu_e = 1{\cdot}60 \times 10^{-25} + 5{\cdot}5 \times 10^{-32} Z^3$ given by Kohlrausch on p. 115 of *Probleme der γ-Strahlung*.

If the value of μ_e is taken as $1{\cdot}56 \times 10^{-25}$, the effective wave-length of the γ-rays from Ra (B + C) filtered by 1·6 cm. of lead can be calculated from the Klein and Nishina formula, and the value found is 7·0 X.U. This wave-length agrees with the conclusion of Gray and Cave* that the γ-rays from Ra (B + C) filtered by 1·61 cm. of lead must have an effective wave-length which is less than 8 X.U. and must be nearer 7 than 8 X.U. Meitner and Hupfeld, from their results in carbon and aluminium, calculate that the effective wave-length of the rays, filtered by 4 cm. of lead, is 6·7 X.U.

Meitner and Hupfeld found that the absorption per electron for γ-rays of wave-length 4·7 X.U.† was not constant even for the lighter elements but increased continually with Z. To account for their results, they found it necessary to take into consideration a nuclear scattering term. For the γ-rays here employed, of wave-length 7·0 X.U., this process does not appear to be significant. On the other hand, Meitner and Hupfeld consider that when the effective wave-length is 6·7 X.U.‡ the photoelectric term is not more than 10 per cent of the total absorption.

The lead filtering necessary for the γ-rays from Ra (B + C) to be exponentially absorbed. The absorption per electron found for lead is $1{\cdot}95 \times 10^{-25}$. As mentioned above, this can be split up into two terms, one due to scattering in terms of the Klein and Nishina formula and the other due to photoelectric absorption. For the first the value found is $1{\cdot}56 \times 10^{-25}$, the corresponding wave-length is 7·0 X.U. and the photoelectric term is $0{\cdot}39 \times 10^{-25}$. To find the absorption for other wave-lengths in lead the variation of both these terms with wave-length has to be considered. The Klein and Nishina formula itself gives the necessary variation for the first term, but an assumption must be made as to the variation of the photoelectric term with wave-length. In the X-ray region the λ^3 law holds, at least approximately, but in the γ-ray region no definite exponent of λ has yet been established. Ellis and Aston§ consider that the exponent is less than 3. Gray and Cave‖ consider that the exponent is of the order 2·05. If a value of 2·2 is assumed, the photoelectric term for the absorption in lead corresponding to any wave-length λ expressed in X.U. will be $0{\cdot}39\,(\lambda/7{\cdot}0)^{2{\cdot}2}$. The validity of this assumption can be tested by calculating the values of μ for the shortest X-rays and comparing it with the values experimentally found. Allen¶ found for λ 81 X.U. in lead that $\mu = 28{\cdot}8$ cm.$^{-1}$ and for λ 126 X.U., $\mu = 59{\cdot}3$ cm.$^{-1}$ For these wave-lengths the Klein and Nishina term is only 5 per cent and 2 per cent respectively of the photoelectric terms, and the values of μ for the sum of the two terms are 24·2 cm.$^{-1}$ and 62·8 cm.$^{-1}$ respectively. While the agreement is not as close as could be wished, it is satisfactory since the calculated value depends mainly on the photoelectric term, which is obtained from the difference between two experimentally determined quantities,

* J. A. Gray and H. M. Cave, *Proc. R.S. Canada*, **21**, 163 (1927).
† Source Th (B + C + C″) filtered by 4 cm. of lead.
‡ The filtered rays from Ra (B + C).
§ C. D. Ellis and G. H. Aston, *Proc. R.S.* **129**, 180 (1930).
‖ J. A. Gray and H. M. Cave, *loc. cit.*
¶ S. J. Allen, *Phys. Rev.* **27**, 266 (1926).

viz. the value of μ_e for lead and that for the lighter elements. On the other hand, if the assumption is correct and there is no other method of absorption other than the two mentioned, it should account for the absorption in lead found by Meitner and Hupfeld* for wave-length 4·7 X.U. For this wave-length the scattering term is $1{\cdot}235 \times 10^{-25}$, and if the above variation with wave-length be used, the photo-electric term is $0{\cdot}162 \times 10^{-25}$. The total absorption per electron would thus be $1{\cdot}40 \times 10^{-25}$, whereas the experimentally found value was $1{\cdot}74 \times 10^{-25}$. The validity of the formula, with regard to the variation with wave-length, therefore, rests on the approximate agreement obtained with the absorption for the short-wave-length X-rays.

If this law of absorption is valid, the variations in intensity of the different wave-lengths of the γ-rays from Ra (B + C), when they pass through 1·6 cm. of lead, can be calculated. The formula can be expressed in the form

$$\mu_e = \sigma_{KN} + 0{\cdot}39\,(\lambda/7{\cdot}0)^{2\cdot2},$$

σ_{KN}

where σ_{KN} represents the Klein and Nishina term. From this the value of μ for 24·2 X.U. is 2·6 cm.$^{-1}$ and therefore γ-rays of this wave-length would be reduced to 1·5 per cent of their intensity in passing through 1·6 cm. of lead. γ-rays of longer wave-length would be reduced to negligible intensity in passing through this thickness. Thus the intense γ-rays in the Ra (B) spectrum of wave-lengths 50·8, 41·6 and 34·9 X.U.† would all be absorbed. The most intense lines in the Ra (C) spectrum according to Ellis and Aston are set out in table 3. The table also gives the intensities of the lines, the values of μ_e calculated with the above formula, the corresponding values of μ, and the calculated intensities after the γ-rays have passed through 1·5 cm. of lead.

Table 3. Intensity of the γ-rays from Ra (C) filtered by 1·6 cm. of lead.

Wave-length (X.U.)	Intensity (Ellis and Aston)	$\mu_e \times 10^{25}$	μ (cm.$^{-1}$)	Emergent intensity
20·2	0·658	6·66	1·82	0·0360
16·0	0·065	4·76	1·30	0·0087
13·1	0·067	3·67	1·00	0·0146
10·9	0·206	2·99	0·817	0·0558
9·89	0·063	2·71	0·742	0·0193
8·89	0·064	2·43	0·665	0·0221
6·94	0·258	1·94	0·530	0·1183
5·57	0·074	1·64	0·448	0·0352

It will be seen from this table that, whereas initially the γ-rays of wave-length 20·2 X.U. are nearly three times as intense as the next strongest line of 6·94 X.U., after passing through 1·6 cm. of lead the strongest line is 6·94 X.U., the next strongest is 10·9 X.U. which has 47 per cent of its intensity, while the γ-ray 20·2 X.U. is only 30 per cent of the intensity of the line 6·94 X.U., the line 5·37 being also of this

* Lise Meitner and H. H. Hupfeld, *loc. cit.*

† C. D. Ellis and G. H. Aston, *loc. cit.*

intensity*. It has now to be decided whether or not the intensities of the γ-rays, as shown in the last column of table 3, are consistent with the effective wave-length of 7·0 X.U.; i.e. whether the average absorption coefficient of the γ-rays, calculated from the sums of the incident and emergent intensities for the individual rays, is consistent with that actually measured. Unfortunately, as the variation of photographic action with wave-length is not known, the calculation cannot be done with accuracy. Further, γ-rays of shorter wave-length than those given in the table have been reported: e.g. Steadman† measured eight γ-rays of considerable intensity and of wave-length shorter than those given in table 3. It is not possible, however, to find an accurate effective wave-length of γ-rays merely by considering the initial intensity of the lines and the absorption of the individual lines in passing through different thicknesses of absorber. If it were possible, the absorption coefficient in lead would steadily decrease as greater thicknesses of lead were employed, for with additional thicknesses the longer wave-lengths would be gradually reduced to negligible intensity, the effective wave-length would decrease and so, in consequence, would the absorption. In contrast to this, it has been previously found‡ that the value of the absorption coefficient is constant for thicknesses of lead between 1·4 and 8·0 cm. There must, in consequence, be a softening process of the harder rays, as they pass through the absorber, so that exponential absorption represents an equilibrium between the reduction in intensity of the longer-wave-length γ-rays and an increasing degradation of the wave-length of the shorter ones.

The conclusion that filtering by 1·4 cm. of lead, with the apparatus used, is sufficient to produce exponential absorption has been supported by measuring the absorption of the γ-rays unfiltered by lead in carbon, aluminium, copper and tin. It was found that the absorption was exponential after a thickness for carbon of 7·5 cm., for aluminium 6 cm., for copper 2·0 cm. and for tin 2·5 cm. When the densities of these substances are considered together with the density of lead, it is found that they are consistent among themselves, since $d \times \rho$ is nearly constant, where d is the thickness required to produce exponential absorption and ρ is the density. d, ρ

Brommer§ examined the absorption in mercury of the γ-rays from Ra (B + C) by placing the source along the axes and near the centres of brass or glass cylinders containing mercury. The γ-rays were measured in an ionization vessel faced with 3 mm. of lead. He found that the absorption was exponential throughout, but as the smallest thickness of mercury was 3·6 mm., the filtering used amounted to the equivalent of 7·4 mm. of lead, i.e. a smaller thickness than was found necessary

* It should be noted that the values have been calculated by assuming that the lead filter was 1·6 cm. thick, whereas the actual filter-thickness was 1·42 cm., the other 0·18 cm. being an allowance for the thickness of the aluminium film-holder and the thickness of the wall of the glass tube containing the radium salt. The laws governing the absorption of the last two substances are not exactly the same as for lead, but the error introduced by the assumption made does not alter the general trend of the argument, nor is the error introduced very great.

† Luville T. Steadman, *Phys. Rev.* **36**, 460 (1930).

‡ J. S. Rogers, *loc. cit.*

§ A. Brommer, *Wien. Ber.* **121**, 1563 (1912); *Phys. Z.* **13**, 1037 (1912).

in these experiments. The value of μ for mercury found by him was 0·641 cm.$^{-1}$ as compared with the value found here of 0·628 cm.$^{-1}$

Effect of using a limiting channel before the absorbers. The effect of introducing a limiting channel between the source and the absorbers has been described above. As a result of this it would appear that the radiation measured by Kohlrausch, which had μ equal to 1·49 cm.$^{-1}$, does not arise from the source directly but is formed by the γ-rays which encounter the walls of the limiting channel being re-scattered into the main beam. If the variation with wave-length of μ, given above is valid, an absorption coefficient of 1·49 cm.$^{-1}$ in lead corresponds to a wave-length of 17 X.U. It is therefore necessary to account for a radiation of effective wave-length 7 X.U. being changed in part to one of effective wave-length 17 X.U.

θ To do this the Compton formula for a γ-ray scattered at angle θ gives the change $\delta\lambda$ of wave-length thus:

$$\delta\lambda = 24{\cdot}2\,(1 - \cos\theta).$$

The intensity of the radiation scattered at angle θ is given by Klein and Nishina.

F According to them, the fraction F of the incident energy scattered per unit solid angle per electron in a direction θ is given by

$$F = \frac{e^4}{2m^2c^4}\,\frac{1+\cos^2\theta}{\{1+\alpha\,(1-\cos\theta)\}^3}\left[1+\frac{\alpha^2\,(1-\cos\theta)^2}{(1+\cos^2\theta)\,\{1+\alpha\,(1-\cos\theta)\}}\right].$$

In table 4 are set out for different angles the wave-length of the γ-rays of 7 X.U. scattered at various angles (Compton relation) and the relative intensity of the radiation at these angles (Klein and Nishina relation).

Table 4. Wave-length and intensity of γ-rays of 7 X.U. scattered at various angles.

Angle (degrees)	Wave-length (X.U.)	Relative intensity
0	7·0	1
5	7·09	0·957
30	10·23	0·298
60	19·1	0·052
90	31·2	0·018

It will be seen from the table that the scattering must be at large angles before the necessary change of wave-length can be produced, as small-angle scattering would not be adequate to account for it. The intensity of the radiation scattered at large angles is however small: at 60° it is some 5 per cent of that scattered at 5°. When a limiting channel has been used, generally the source has been pushed up very close to one end, so that the intensity of the γ-rays from the source falling on this near end of the channel is very much greater than that at the far end. Further, it is just at this near end that the γ-rays can be scattered at large angles and sent into the beam proceeding to the absorbers. Thus although the fractional intensity of the rays scattered at large angles is small, in view of the much greater intensity of the γ-rays falling so that they could be scattered at large angles, it

would appear that, qualitatively, account can be given of the softening effect produced by the scattering of γ-rays by the channel walls.

Various experimental determinations of absorption coefficients will now be examined to see to what extent they support this argument. In the first place the same softening was observed above whether a lead channel 2·5 cm. long was used or a copper one 4·1 cm. long, and approximately the same softening was observed by Kohlrausch with a channel 12 cm. long; but although the lengths of the channels were so different, in all three the conditions would be approximately the same at the source end of the channel, where the greatest change in wave-length would be expected. Next, Meitner and Hupfeld used a channel 36 cm. long and 1·2 × 1·0 cm. in cross-section, but their source was placed back from the near end of the channel so that there was no opportunity for the very intense radiation to produce large-angle scattering into the main beam. They found that the same values of the absorption coefficients were obtained whether the absorbers were placed at the near end or at the far end of the channel; this showed that the experimental conditions were such that there was no softening of the radiation in its passage down the channel. Further they found that, for Th (B + C + C″), 1 cm. of lead filtering produced the same absorption coefficients as 4 cm., while Chao* with a filter of 1·36 cm. of lead found that $\mu = 0{\cdot}565$ cm^{-1}, and with 6·8 cm. that $\mu = 0{\cdot}477$. In Chao's apparatus, however, the conditions were such that large-angle scattering could occur close to the source, and hence the apparent discrepancies between the two sets of results are accounted for.

Ahmad†, in order to use small sources, employed a comparatively wide-angle beam and made allowance for scattering, except the scattering produced at the walls of the channel. The amount of scattered radiation that would be sent into the main beam with such a wide channel would be considerable, and hence the values of μ due to the greater proportion of softer radiation were greater than those found by Kohlrausch or by the author. Thus with filtering of 3·41 cm. of mercury, he found μ_e for lead to be $2{\cdot}540 \times 10^{-25}$. Owen, Fleming and Fage‡ placed their source in a small cylindrical hole so that it was possible for high-angle scattering radiation from the walls of the hole to enter the main beam. The amount of this radiation was apparently considerable, as is shown by their high value of μ, which was 0·720 cm^{-1} for the γ-rays from Ra (B + C) filtered with 2·3 cm. of lead. Gray and Cave§ used two arrangements, in both of which there were γ-rays scattered at large angles near the source, but in one of these they used a limiting channel through which the rays passed before they encountered the absorbers. The values of μ/ρ obtained with this arrangement were always higher than those in the absence of this limiting channel, as table 5 shows.

Although the differences obtained were not great, being at most 4 per cent, they were always in such a direction as to indicate the softening of the radiation

* C. Y. Chao, *Proc. Nat. Acad. Sci.* **16**, 431 (1930).
† N. Ahmad, *Proc. R.S.* **105**, 507 (1924); **109**, 206 (1925).
‡ E. A. Owen, N. Fleming and Winifred E. Fage, *Proc. Phys. Soc.* **36**, 355 (1924).
§ J. A. Gray and H. M. Cave, *loc. cit.*

at the walls of the channel. The amount of softening to be expected in these experiments would not be great, as the channel was not placed next to the source and hence the scattering would be confined to smaller angles. Attention has already been drawn by L. H. Gray* to the softening of γ-rays by scattering at the walls of a channel.

Table 5. Values of μ/ρ obtained by Gray and Cave.

Filter thickness (cm. of lead)	μ/ρ			
	Lead		Copper	
	without channel	with channel	without channel	with channel
2·2	0·0530	0·0552	0·0470	0·0479
3·25	0·0502	0·0513	0·0455	0·0460
4·30	0·0478	0·0487	0·0448	0·0452

§ 7. CONCLUSIONS

(*a*) The absorption coefficients of 22 elements for the γ-rays from Ra (B – C) filtered by 1·6 cm. of lead have been measured by a photographic method.

(*b*) For elements up to $Z = 30$ the absorption per electron is constant, in agreement with the Klein-Nishina formula, and has the value $1{\cdot}56 \times 10^{-25}$. This value corresponds to a wave-length 7·0 X.U.

(*c*) For values of Z greater than 30, μ_e increases continually with Z so that $\mu_e = 1{\cdot}56 \times 10^{-25} + 7{\cdot}1 \times 10^{-32} Z^3$.

(*d*) On account of the Z^3 variation it is assumed that the extra absorption for the heavier elements is due to a photoelectric term.

(*e*) Both the Klein-Nishina term and the photoelectric term must be separately considered in calculating the variation of μ_e with wave-length. It has been assumed that the second of these varies as $\lambda^{2\cdot2}$.

(*f*) The absorption per electron can be expressed thus:

$$\mu_e = \sigma_{KN} + 7{\cdot}1 \times 10^{-32} \times 0{\cdot}39 \left(\frac{\lambda}{7{\cdot}0}\right)^{2\cdot2} Z^3$$
$$= \sigma_{KN} + 3{\cdot}83 \times 10^{-34} \lambda^{2\cdot2} Z^3.$$

(*g*) The limiting channel generally used in absorption experiments to limit the γ-rays before they fall on the absorbers has been shown to cause the main beam to receive a certain amount of scattered and softened γ-radiation.

§ 8. ACKNOWLEDGMENTS

These experiments were carried out in the Commonwealth Radium Laboratory, University of Melbourne. The author wishes to express his thanks to Mr A. H. Turner, M.Sc., Physicist of that laboratory for making available its facilities. He also wishes to acknowledge his indebtedness to Prof. T. H. Laby, F.R.S. for assistance in preparing the paper.

* L. H. Gray, *Proc. R.S.* **128**, 361 (1930).

DISCUSSION

Dr G. H. Aston. The author finds that a $\lambda^{2\cdot 2}$ law for the photoelectric absorption of γ-rays enables him to deduce approximately correct values for the absorption in the X-ray region. It is probable, however, that if the photoelectric absorption were to be measured for a different effective γ-ray wave-length, a different power of λ would be required to give the right value in the X-ray region. It is unlikely that a simple power law can be used to represent the photoelectric absorption in the γ-ray region. An empirical formula for this absorption should agree with the X-ray measurements not only in magnitude but also in slope. L. H. Gray* has deduced such a formula, using data from absorption and intensity-measurements of γ-rays.

* *Proc. Camb. Phil. Soc.* **27**, 103 (1931).

THE DERIVATION OF MAXWELL'S EQUATIONS FROM THE EQUATIONS OF THE QUANTUM THEORY

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Communicated by Prof. W. Wilson, F.R.S., March 4, 1932.
Read March 18, 1932

ABSTRACT. In a theory developed by Flint and Fisher the fundamental equations of the quantum theory are expressed in terms of a five-dimensional geometry based upon the use of two inter-related tensors A and B. In the present paper Maxwell's equations are derived from the five-dimensional equations previously proposed, and the tensors A and B are exhibited as geometrical quantities related to the electromagnetic potential.

In their attempt to develop a unitary physical theory to include the fundamental equations of the quantum theory, Flint and Fisher*, by making certain modifications of the five-dimensional geometrical scheme of Kaluza and Klein, have been led to an equation of the form

$$\operatorname{div} A = 0 \qquad \ldots\ldots(1),$$

A where A is a contravariant tensor of the second rank.

They express the opinion that this tensor has some geometrical or metrical significance, but the actual meaning remains at present undiscovered. The equation (1) is interpreted in accordance with the metrical scheme proposed and leads directly to Dirac's equations without any artificial introduction of operators.

In a later paper† it has been shown that the occurrence of positive and negative charges and the asymmetry in the masses of the proton and electron can be accounted for in terms of geometry and metrics.

The work of Kaluza and Klein and later of de Broglie has shown that in the five-dimensional system the tracks of all particles in gravitational and electromagnetic fields are geodesics. The work of Flint and Fisher shows that the geodesics are null geodesics and that the generalized mass of all particles is zero. Thus the analogy with the track of a ray of light in the space-time of Einstein is complete and, as has been stated before, this may well form the basis of a wave-theory of matter. The occurrence of mass in physics is due, according to this theory, to our description of phenomena in space and time.

The theory points to the fundamental character of the tensor A of equation (1) and it is important to follow up any line of study which will indicate its meaning. The author has previously studied this question‡ and has shown a connection between the components of electronic magnetic and electric moments. The procedure adopted led to results analogous to those obtained by Dirac.

* *Proc. R.S.* A, **126**, 644 (1930).
† *Proc. R.S.* A, **131**, 170 (1931).
‡ *Proc. Phys. Soc.* **43**, 124 (1931).

In the original paper on this subject† two tensors A and B were introduced but there exist a number of relations between the components of the two tensors, so that actually one fundamental tensor alone is introduced. These conditions were adopted by analogy with the usual procedure in the relativistic treatment of Maxwell's equations, and also in order to show that the work was able to account for previous suggestions made by other writers. *B*

The present purpose is twofold. Firstly we show that Maxwell's equations can be derived by simple combinations of the fundamental equations proposed, and secondly by developing the relations between the electric and magnetic intensities and the tensors A and B we connect these tensors with geometrical quantities, for the electromagnetic potential is in this scheme a geometrical quantity and the intensities are derived from it.

The equations proposed‡ are

$$\frac{\partial A^{mn}}{\partial x^n} = -\frac{\partial \psi_0}{\partial x^m} + \frac{2\pi ie}{h}\phi_n A^{mn} + \frac{2\pi ie}{h}\phi_m \psi_0 - \frac{2\pi imc}{h} A^{m5} \quad \text{.....(2),} \qquad \theta, \phi, \psi$$

and

$$\frac{\partial B^{mn}}{\partial x^n} = -\frac{\partial \theta_0}{\partial x^m} + \frac{2\pi ie}{h}\phi_n B^{mn} + \frac{2\pi ie}{h}\phi_m \theta_0 - \frac{2\pi imc}{h} B^{m5} \quad \text{.....(3).}$$

The conjugate equation of (1) is

$$\frac{\partial A^{*mn}}{\partial x^n} = -\frac{\partial \psi_0^*}{\partial x^m} - \frac{2\pi ie}{h}\phi_n A^{*mn} - \frac{2\pi ie}{h}\phi_m \psi_0^* + \frac{2\pi imc}{h} A^{*m5} \quad \text{.....(2*).}$$

To obtain the set of equations corresponding to

$$\frac{1}{c}\frac{\partial H}{\partial t} + \operatorname{curl} E = 0 \quad \text{.....(4),} \qquad H, E$$

and

$$\operatorname{div} H = 0 \quad \text{.....(5),}$$

we multiply the equation (2) by A^{*mk} and the equation (2*) by A^{mk} and subtract.

We obtain

$$\left(A^{*mk}\frac{\partial A^{mn}}{\partial x^n} - A^{mk}\frac{\partial A^{*mn}}{\partial x^n}\right)$$

$$= -\left(A^{*mk}\frac{\partial \psi_0}{\partial x^m} - A^{mk}\frac{\partial \psi_0^*}{\partial x^m}\right) + \frac{2\pi ie}{h}\phi_n\left(A^{*mk}A^{mn} + A^{mk}A^{*mn}\right)$$

$$+ \frac{2\pi ie}{h}\phi_m\left(A^{*mk}\psi_0 + A^{mk}\psi_0^*\right) - \frac{2\pi imc}{h}\left(A^{*mk}A^{m5} + A^{mk}A^{*m5}\right),$$

or $\dfrac{\partial}{\partial x^n}\left(A^{*mk}A^{mn} - A^{mk}A^{*mn}\right)$

$$= A^{mn}\frac{\partial A^{*mk}}{\partial x^n} - A^{*mn}\frac{\partial A^{mk}}{\partial x^n} - A^{*mk}\frac{\partial \psi_0}{\partial x^m} + A^{mk}\frac{\partial \psi_0^*}{\partial x^m}$$

$$+ \frac{2\pi ie}{h}\phi_n\left(A^{*mk}A^{mn} + A^{mk}A^{*mn} + A^{*nk}\psi_0 + A^{nk}\psi_0^*\right)$$

$$- \frac{2\pi imc}{h}\left(A^{*mk}A^{m5} + A^{mk}A^{*m5}\right) \quad \text{.....(6).}$$

† *Proc. R.S.* A, **126**, 644 (1930). ‡ *Ibid.*, p. 650.

Putting k equal to 4 in equation (6), we obtain the following equation:

$$\frac{1}{c}\frac{\partial}{\partial t}i(A^{*m4}A^{m1}-A^{m4}A^{*m1})+\frac{\partial}{\partial x^2}(A^{*m1}A^{m2}-A^{m1}A^{*m2})-\frac{\partial}{\partial x^3}(A^{*m3}A^{m1}-A^{m3}A^{*m1})$$

$$=\left(A^{mn}\frac{\partial A^{*m1}}{\partial x^n}-A^{*mn}\frac{\partial A^{m1}}{\partial x^n}-A^{*m1}\frac{\partial \psi_0}{\partial x^m}+A^{m1}\frac{\partial \psi_0^*}{\partial x^m}\right)$$

$$+\frac{2\pi ie}{h}\phi_n(A^{*m1}A^{mn}+A^{m1}A^{*mn}+A^{*n1}\psi_0+A^{n1}\psi_0^*)$$

X_1 $$-\frac{2\pi imc}{h}(A^{*m1}A^{m5}+A^{m1}A^{*m5})=X_1 \text{ (say)} \qquad \text{.....(6·1).}$$

Equation (6·1) suggests a comparison with

$$\frac{1}{c}\frac{\partial H_1}{\partial t}+\frac{\partial E_3}{\partial x^2}-\frac{\partial E_2}{\partial x^3}=0,$$

and thus we may write

$$E_3=ai(A^{*m3}A^{m1}-A^{m3}A^{*m1}), \quad E_2=a(A^{*m1}A^{m2}-A^{*m2}A^{m1}),$$

$$H_1=a(A^{*m1}A^{m4}-A^{*m4}A^{m1}),$$

where a is a constant factor.

Similarly

$$E_1=ai(A^{*m2}A^{m3}-A^{m2}A^{*m3}), \quad H_2=a(A^{*m2}A^{m4}-A^{*m4}A^{m2}),$$

$$H_3=a(A^{*m3}A^{m4}-A^{*m4}A^{m3}).$$

The quantity on the right of equation (6·1) may be regarded as representing a

σ_1 component of magnetic current and if we denote this current component by σ_1 we have

$$\sigma_1=aciX_1.$$

Writing $k=4$, we obtain

$$\frac{\partial}{\partial x^n}(A^{*m4}A^{mn}-A^{m4}A^{*mn})=X_4,$$

X_4 where X_4 denotes the right-hand side of (6) with k equal to 4.

If this is compared with (5), we can write

$$H_n=a(A^{*mn}A^{m4}-A^{*m4}A^{mn}).$$

The condition, $X_4=0$, is suggested but recent developments indicate that free magnetic charges are not excluded by the quantum theory. In order to take into consideration the possibility that (5) should be extended to

$$\text{div } H=\sigma,$$

we write

$$aX_4=-\sigma.$$

The other group of Maxwell's equations is

$$-\frac{1}{c}\frac{\partial E}{\partial t}+\text{curl } H=\frac{j}{c} \qquad \text{.....(7),}$$

and

$$\text{div } E=\rho \qquad \text{.....(8),}$$

j, ρ where j is the electric current vector and ρ the density of charge.

To obtain the corresponding equations from the quantum equations, we multiply (3) by A^{*mk} and (2*) by B^{*mk} and subtract.

We obtain

$$\frac{\partial}{\partial x^n}(A^{*mk}B^{mn} - B^{*mk}A^{mn}) = \left(B^{mn}\frac{\partial A^{*mk}}{\partial x^n} - A^{mn}\frac{\partial B^{*mk}}{\partial x^n} - A^{*mk}\frac{\partial \theta_0}{\partial x^m} + B^{*mk}\frac{\partial \psi_0}{\partial x^m}\right)$$
$$+\frac{2\pi ie}{h}\phi_n(A^{*mk}B^{mn} - B^{*mk}A^{mn} + A^{*nk}\theta_0 - B^{*nk}\psi_0)$$
$$-\frac{2\pi imc}{h}(A^{*mk}B^{m5} - B^{*mk}A^{m5}) \qquad \ldots\ldots(9).$$

By inserting the value $k = 1$, we obtain on the left-hand side

$$\frac{\partial}{\partial x^2}(A^{*m1}B^{m2} - B^{*m1}A^{m2}) + \frac{\partial}{\partial x^3}(A^{*m1}B^{m3} - B^{*m1}A^{m3})$$
$$+\frac{1}{c}\frac{\partial}{\partial t}\cdot\frac{A^{*m1}B^{m4} - B^{*m1}A^{m4}}{i}.$$

This should be compared with the left-hand side of the equation

$$\frac{\partial H_3}{\partial x^2} - \frac{\partial H_2}{\partial x^3} - \frac{1}{c}\frac{\partial E_1}{\partial t} = \frac{j_1}{c},$$

and if we regard the equations as identical we can write

$$E_1 = a(A^{*m1}B^{m4} - B^{*m1}A^{m4}), \quad H_2 = ai(A^{*m1}B^{m3} - B^{*m1}A^{m3}),$$
$$H_3 = ai(B^{*m1}A^{m2} - A^{*m1}B^{m2}).$$

Similarly we obtain

$$E_2 = a(A^{*m2}B^{m4} - B^{*m2}A^{m4}), \quad H_1 = ai(B^{*m2}A^{m3} - A^{*m2}B^{m3}),$$

and

$$E_3 = a(A^{*m3}B^{m4} - B^{*m3}A^{m4}).$$

If we denote the right-hand side of equation (9) by Y_k, we have Y_k

$$j_k = -aicY_k.$$

Writing $k = 4$ we obtain

$$\frac{\partial}{\partial x^n}(A^{*m4}B^{mn} - B^{*m4}A^{mn}) = Y_4,$$

where Y_4 denotes the right-hand side in this case. Y_4

We may then compare this equation with (8) and write

$$E_n = a(B^{*m4}A^{mn} - A^{*m4}B^{mn}),$$

and

$$\rho = -aY_4.$$

We have thus obtained three different forms for the intensities and it remains to show that they are equal to one another. We proceed to show that this is the case for E_1 and the rest follows by symmetry. The demonstration of the identity of these various forms for the intensities rests upon certain relations adopted in the paper already referred to†. These relations are:

$$A^{23} = iB^{41}, \quad A^{31} = iB^{42}, \quad A^{12} = iB^{43},$$
$$A^{41} = iB^{23}, \quad A^{42} = iB^{31}, \quad A^{43} = iB^{12},$$

† Flint and Fisher, *loc. cit.* p. 651.

and they were adopted by analogy with Maxwell's equations as mentioned above. The relations lead in a remarkable way from the general equation proposed in that paper to the first-order equations of the quantum theory.

We have obtained the following expressions for E_1:

$$a\,(A^{*m1}B^{m4} - B^{*m1}A^{m4}), \quad a\,(B^{*m4}A^{m1} - A^{*m4}B^{m1}),$$
$$ai\,(A^{*m2}A^{m3} - A^{m2}A^{*m3}).$$

By expansion of the first of these (m having the values 2 and 3 only since the components with both affixes the same vanish), and by replacing the A-components by B-components and *vice versa*, we see at once that the first expression is equal to the second. The first may be shown to be equal to the third by replacing the B-components by A-components.

We thus obtain the following expressions for the electric and magnetic components of field intensity:

$$\begin{aligned} E_1 &= a\,(A^{*m1}B^{m4} - B^{*m1}A^{m4}) = a\,(B^{*m4}A^{m1} - A^{*m4}B^{m1}) \\ &= ai\,(A^{*m2}A^{m3} - A^{m2}A^{*m3}), \\ H_1 &= ai\,(B^{*m2}A^{m3} - A^{*m2}B^{m3}) = ai\,(A^{*m3}B^{m2} - B^{*m3}A^{m2}) \\ &= a\,(A^{*m1}A^{m4} - A^{*m4}A^{m1}), \end{aligned}$$

with corresponding expressions for E_2, E_3, and H_2, H_3. The expressions for the current are

$$j_k = -aicY_k,$$

and for the density of charge

$$\rho = -aY_4;$$

while for the magnetic current we have

$$\sigma_k = aicX_k,$$

and for the magnetic density

$$\sigma = -aX_4.$$

The values of the X's and Y's have been indicated above and need not be re-written.

It is noteworthy that the same relations which are indicated by the analogy referred to and which lead directly to the results required in the quantum theory, should be exactly what is required in the present discussion. The components of field-intensity are derivable from the electromagnetic potential, which in this theory is a geometric quantity like the g's of the relativity theory. Through the field components the A's and B's are thus related to the electromagnetic potential and so to the geometry. The relation does not appear to be very simple but the result verifies the suggestion referred to at the beginning of this paper that A and B have a geometrical significance.

This is important from the point of view of a unitary theory, for Flint's work has shown that it is possible to include in a geometrical and metrical scheme the physical realms of gravitation, electromagnetism and the quantum theory. Moreover, in this scheme only one constant, e, occurs, positive and negative values of e

being related to a directional property while the asymmetry of electronic and protonic masses is accounted for by consideration of scales, which follow from an extension of the theory of Weyl and Eddington.

The present paper may be compared with those of other writers on this subject, especially with two papers by Proca† and v. Wisniewski‡.

In conclusion I take the opportunity of expressing my thanks to Dr H. T. Flint for suggesting this line of research to me and for help and advice in carrying it out.

† *J. de Phys.* **1**, 235 (1930).

‡ *Z. f. Phys.* **66**, 697 (1930).

SIR A. S. EDDINGTON'S RECENT THEORIES

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Received December 24, 1931. *Read and discussed February* 19, 1932

ABSTRACT. The significance of Sir A. S. Eddington's work on the fine-structure constant $2\pi e^2/hc$, the ratio of masses of proton and electron M_P/m, and on the cosmical constant, is outlined. The experimental verification of his theory of the packing effect and of the rate of recession of spiral nebulae is mentioned. His predictions that $hc/2\pi e^2 = 137$ and $M_P/m = 1847{\cdot}60$ are considered in detail. The only evidence against these predictions is that given by four recent experiments, which indicate that $e/m = 1{\cdot}761 \times 10^7$ e.m.u. Reasons are given for believing that this value is too low, and that Eddington's predictions are consistent with experiment. It is unlikely that *both* his predictions require correction terms of the order 1 part in 1847 and it is shown that if $M_P/m = 1847{\cdot}60$, then

$$hc/2\pi e^2 = (137 - 0{\cdot}02_7) \pm (0{\cdot}01_9 \pm 0{\cdot}00_2).$$

Hence it is shown that the theory of 137 is probably *exactly* correct. Similarly, it is shown that if $hc/2\pi e^2 = 137$, then

$$M_P/m = (1847{\cdot}60 - 0{\cdot}5_9) \pm (0{\cdot}5_1 \pm 0{\cdot}0_5),$$

and thus Eddington's prediction for M_P/m might be too great by as much as unity. (These final calculations do not depend on any experimental determinations of e/m.) Consequences of the theories are mentioned. The value of the electronic charge is about $(4{\cdot}777_5 \pm 0{\cdot}001) \times 10^{-10}$ e.s.u., differing from the Millikan-Birge estimate by about as much as might be expected when regard is had to the probable error of the latter.

§ 1. INTRODUCTION

During the last few years Sir Arthur Eddington has developed theories which predict relationships between some of the most important universal constants in physics. It is my purpose, in this paper, to discuss the experimental evidence supporting these theories, to point out their general significance, and to outline some of their consequences. Sir Arthur's theories, which concern the "meeting-ground of astronomy, relativity and wave-mechanics," are abstruse, and can only be properly studied by reference to the original papers*.

§ 2. THE GENERAL SIGNIFICANCE OF THE THEORIES

In order to understand the significance of these theories, we may consider briefly the way in which physics has developed. Progress has been made not only by observation and experiment, but also by the summarizing of the results in the form of "laws of nature." It is only by the formulation of general laws that we

* A. S. Eddington, *Proc. R.S.* A, **122**, 358 (1929); *Nature*, **124**, 840 (1929); *Proc. R.S.* A, **131**, 696 (1930); *Proc. Camb. Phil. Soc.* **27**, 18 (1931); *Proc. R.S.* A, **133**, 605 (1931); *Proc. Phys. Soc.* **44**, 1 (1932); *Proc. R.S.* A, **134**, 524 (1931).

are enabled to think rationally about such a vast amount of experimental knowledge. It has been claimed that there is a large *a priori* probability of the laws being simple in form*, and natural philosophers, such as Faraday and Joule, were almost convinced that there was a unity underlying all natural phenomena.

The amount of experimental knowledge of inanimate nature is continually increasing, but at present a large part of it can be correlated by general laws. In one respect, however, the unification lacked completion. Relativity interpreted gravitation, but did not predict the value of the universal gravitational constant. Indeed it introduced new constants, such as the number of protons in the "world." Similarly, the quantum theory introduced a new constant, Planck's constant of action h.

The only way in which the values of such universal constants can be predicted is by showing that they are related to other universal constants. We cannot, for instance, predict the mass of a proton in grams, for that would be equivalent to predicting the number of protons in the kilogram. But it may be possible to predict from general experimental knowledge the ratio of the masses of proton and electron. The matter may be expressed more generally by saying that non-dimensional products or quotients of the universal constants may be discovered to have numerical values that can be expressed in a simple mathematical way.

In recent years many attempts have been made to find such relationships†. Most of these attempts have had little theoretical basis, and many have definitely disagreed with experiment. Nevertheless, there was reason to expect that such relationships would eventually be found, because many similar ones had been established in the past. For example, Rydberg's, Stefan's and Wien's constants were known to be related to Planck's constant.

The situation is now changed. The theories that Sir Arthur Eddington has developed have predicted three further relationships. These predictions are supported by experimental evidence, and the theories constitute an advance in knowledge quite comparable with that brought about by relativity and the quantum theory. We may note, in passing, that the theories are concerned with the number of degrees of freedom of systems.

§ 3. SIR ARTHUR EDDINGTON'S PREDICTIONS

The three chief relationships deduced by Eddington may be stated thus:

Firstly, $$hc/2\pi e^2 = 137 \qquad \text{.....(1)},$$

where h is Planck's constant, c the velocity of light in a vacuum and e the electronic charge expressed in electrostatic units. h, c, e

Secondly, the ratio of the masses of proton and electron, M_P/m, is equal to the ratio of the roots of the equation M_P, m

$$10x^2 - 136x + 1 = 0,$$

or $$M_P/m = 1847{:}599_5 \qquad \text{.....(2)}.$$

* H. Jeffreys, *Scientific Inference*, pp. 43–51.

† For instance, see G. N. Lewis and E. Q. Adams, *Phys. Rev.* **3**, 92 (1914); R. Fürth, *Phys. Zeit.* **30**, 895 (1929).

Thirdly, $$\{M_P m/(M_P + m)\}\, c^2/e^2 = \sqrt{N/R} \qquad \ldots\ldots(3),$$

N where N is the number of electrons (or protons) in the universe, and the universe
R is of the Lemaître type, having an equilibrium radius R.

§ 4. THE PACKING EFFECT

One numerical test of Eddington's theories was the verification of the prediction, which he made incidentally, that if protons and electrons combined to form a rigid system the mass would be $(1 - 2\pi e^2/hc)$ of the sum of the masses of the constituents considered separately. This prediction of the packing effect in an α-particle, which had previously been suggested on a purely empirical basis by Lunn, was commented on favourably from an experimental point of view by Birge*, whose treatment I will follow.

The experimental value of the atomic weight of hydrogen, relative to a mixture of the oxygen isotopes as 16, may be taken as $1{\cdot}007{,}77 \pm 0{\cdot}000{,}02$, the relative weight of four hydrogen atoms being thus $4{\cdot}031{,}08 \pm 0{\cdot}000{,}08$. Assuming that the helium atom consists of a perfectly rigid α-particle together with two electrons, and applying Eddington's theory, we find the estimated atomic weight of helium to be

$$4{\cdot}001{,}66 \pm 0{\cdot}000{,}08.$$

The value found by chemical methods is

$$4{\cdot}001{,}8 \pm 0{\cdot}000{,}4,$$

and from Aston's work on mass-spectra, corrected for a trace of O_{18}, it is

$$4{\cdot}001{,}8 \pm 0{\cdot}000{,}2.$$

The agreement is thus entirely satisfactory, though the experiments are not accurate enough for this calculation to be used as a test of equation (1).

§ 5. THE THEORY OF 137

In discussing equations (1) and (2) it is best to state at once that the *only* experimental evidence against either prediction is based on certain recent estimates of the specific electronic charge, e/m. This estimate, which Birge† designated the "spectroscopic" estimate, is about $\frac{1}{2}$ per cent lower than the value suggested by the work of other experimenters (Birge's "deflection" estimate). The discrepancy between these two estimates will be discussed later in this paper.

Considering Eddington's theory of 137, equation (1), we find that the value of $hc/2\pi e^2$ was estimated in 1929 by Birge‡ as

$$137{\cdot}29_4 \pm 0{\cdot}11.$$

* R. T. Birge, *Phys. Rev.* **35**, 1015 (1930).
† *Phys. Rev. Supplement*, **1**, 1–73 (1929).
‡ *ad loc.* 71 (1929).

This estimate was based on Birge's estimate of the electronic charge, viz.

$$(4{\cdot}770 \pm 0{\cdot}005) \times 10^{-10} \text{ e.s.u.},$$

derived from a re-calculation of Millikan's experimental results and from the absolute determination of X-ray wave-lengths made by A. P. R. Wadlund. The value of h which Birge used was based on estimates obtained by six methods, but the method to which by far the greatest weight was attributed depended on the estimate of e/m. And Birge here assumed the low or spectroscopic estimate of e/m, to the entire exclusion of his deflection estimate.

Millikan subsequently discussed the problem*, and his final estimate of e was the same as that given by Birge. Millikan concluded that it was "highly improbable" that $hc/2\pi e^2$ could be exactly 137 (or exactly 136, the value Eddington originally suggested).

I have recently shown† that more reliable estimates of e and h can be obtained by an analysis of the experimental results that are usually used to estimate h. My calculation (which can be considered an elaboration of one originally used by Planck) resulted in the estimates

$$e = (4{\cdot}778_9 \pm 0{\cdot}002_9) \times 10^{-10} \text{ e.s.u.},$$

and

$$hc/2\pi e^2 = 137{\cdot}01_7 \pm (0{\cdot}05_9 \pm 0{\cdot}00_5).$$

Taking this estimate of e and the entirely independent estimate given by Birge and by Millikan, and weighting them according to their probable errors, I now obtain

$$e = (4{\cdot}776_4 \pm 0{\cdot}002_5) \times 10^{-10} \text{ e.s.u.},$$

$$h = (6{\cdot}553_5 \pm 0{\cdot}004_7) \times 10^{-27} \text{ erg.-sec.},$$

$$hc/2\pi e^2 = 137{\cdot}05_9 \pm 0{\cdot}05_4.$$

The agreement with Eddington's theory is again very satisfactory.

Prof. Birge has quite recently‡ discussed my calculations, and he agrees that a more reliable estimate of the electronic charge can be obtained by my method than by the direct methods. But he continues to adopt the lower ("spectroscopic") estimate of e/m, to the entire exclusion of the so-called deflection estimate. As a consequence his results disagree with two of Eddington's theories, equations (1) and (2).

I will give my reasons for believing that the value of e/m is not as small as Prof. Birge suggests. The lower or spectroscopic estimate was originally based on H. D. Babcock's work on the Zeeman effect and on that of W. V. Houston on the hydrogen and helium spectra§. Subsequently Perry and Chaffee‖ and Kirchner¶ obtained almost the same value by experiments on cathode rays. These four very

* R. A. Millikan, *Phys. Rev.* **35**, 1233 (1930).
† W. N. Bond, *Phil. Mag.* **10**, 994 (1930); **12**, 632 (1931).
‡ *Bulletin*, Am. Phys. Soc., Dec. 6th, 1931.
§ R. T. Birge, *loc. cit.*, 44–48.
‖ *Phys. Rev.* **36**, 904 (1930).
¶ *Phys. Zeit.* **31**, 1073 (1930); *Ann. d. Physik*, **8**, 975 (1931).

concordant estimates suggest that $e/m = 1{\cdot}761 \times 10^7$ e.m.u. There are, however, about 18 estimates of e/m ranging from $1{\cdot}763$ to $1{\cdot}775 \times 10^7$, suggesting a value of about $1{\cdot}769 \times 10^7$*. The disagreement is more than can be accounted for by the probable errors of the estimates. *Whichever* value we assume, the situation is peculiar. Moreover, we ought not to be guided by the probable errors in deciding between the two values.

We might be satisfied that the earlier determinations by the two spectroscopic methods were in each case too high, and by a similar amount. That the earlier results by the deflection method should have been in error in the same sense, and by about the same amount, seems strange. It has been suggested that the presence of traces of gas in the apparatus caused the results to be too large. But there seems to be no progressive decrease in the successive results, which might have been expected to occur as the technique of high-vacuum work developed. Again, the deflection of β-rays would be expected to give results little affected by this error: but the results so obtained indicate a value of about $1{\cdot}767 \times 10^7$. Further evidence for the higher value is given by Birge's† estimate, based on the Compton effect, of $(1{\cdot}772 \pm 0{\cdot}006) \times 10^7$. Yet again, J. A. Bearden‡ has recently deduced from the refraction of X-rays a value that may be stated as $(1{\cdot}769 \pm 0{\cdot}004) \times 10^7$. Finally, if I omit from my calculations *all* data depending on determinations of e/m, and do not assume either of Eddington's predictions in equations (1) and (2), I obtain the estimates

$$e/m = (1{\cdot}767_5 \pm 0{\cdot}003_1) \times 10^7 \text{ e.m.u.},$$

and

$$hc/2\pi e^2 = 137{\cdot}07 \pm 0{\cdot}12,$$

in good agreement with Eddington's 137.

For all these reasons we can continue to be satisfied with the accuracy of Eddington's theory of 137.

§ 6. THE RELATIVE MASSES OF PROTON AND ELECTRON

Prof. Birge in 1929 gave two estimates of M_p/m based on his spectroscopic and deflection estimates of e/m,

$$(M_p/m)_{\text{spect.}} = 1838{\cdot}_{26} \pm 1,$$

$$(M_p/m)_{\text{defl.}} = 1846{\cdot}_{61} \pm 2.$$

Birge pointed out that these two values definitely disagreed with one another, but he now adopts the spectroscopic or smaller value. I have discussed above my reasons for disagreeing with this estimate.

In my previous work I showed that the experimental evidence for Eddington's 137 was rather greater than that for any one of the other theoretical relationships between e and h, and therefore I assumed the value 137 in the subsequent parts

* See, for instance, Geiger and Scheel's *Handbuch der Physik*, **22**, 81.

† R. T. Birge, *loc. cit.* 58.

‡ *Phys. Rev.* **37**, 1228 (1931).

of my papers. Using Bohr's theory of spectra and Rydberg's constant, I then deduced

$$M_P/m = 1846{\cdot}5_7 \pm 0{\cdot}4_8.$$

This estimate, which agrees with Birge's deflection value, but claims a higher accuracy, is in reasonable agreement with Eddington's 1847·6, the difference being 2·1 times my probable error. It definitely disagreed with Eddington's former suggestion of $136^2/10$, differing from that value by 6·3 times my probable error.

Repeating the calculation, without assuming the 137, but taking into account the Birge-Millikan direct estimate of e as well as my independent estimate, I now obtain

$$M_P/m = 1845{\cdot}_{33} \pm 1{\cdot}3_3.$$

This estimate differs from Eddington's predicted value by 1·7 times my probable error: the agreement may again be considered satisfactory.

§ 7. ARE THESE EQUATIONS EXACTLY CORRECT?

The various estimates of $hc/2\pi e^2$ and M_P/m that I have deduced, and given above, differ from Eddington's predictions by between 0·3 and 2·1 times my probable errors: in other words, experiment and theory differ by from 0·01 to 0·12 per cent. The agreement is, therefore, entirely satisfactory. It may, however, be suggested that there is still the possibility of Eddington's 137 and 1847·60 being found to require correction by about 1 part in 1847. This can be tested further.

We have no experimental reason to expect either correction to be necessary, and it is relatively unlikely that *both* corrections will be needed. Let us therefore assume for the moment that M_P/m is exactly $1847{\cdot}599_5$. I am then able to deduce from the experimental data the estimate

$$hc/2\pi e^2 = (137 - 0{\cdot}02_7) \pm (0{\cdot}01_9 \pm 0{\cdot}00_2).$$

No experimental determinations of e/m are involved here. It follows that the chance of $hc/2\pi e^2$ being as small as $137\,(1 - 1/1847)$ is only 1 in 20, unless the 1847·60 *also* requires correction. Similarly, the chance of it being as great as $137\,(1 + 1/1847)$ is only 1 in 6000, unless *both* the 137 and 1847·60 require correction. As there is little reason to expect two corrections when theory and experiment are already in good agreement, we may conclude that the 137 is not in error by as much as 1 part in 1847. Smaller corrections are not to be expected, and therefore

$$hc/2\pi e^2 = 137$$

may be considered to be exactly correct.

Assuming this, and reversing the procedure, I obtain the estimate

$$M_P/m = (1847{\cdot}599_5 - 0{\cdot}7_9) \pm 0{\cdot}4_6,$$

or, omitting all the data that depend on experimental estimates of e/m (about which there has been discussion), the estimate becomes

$$M_P/m = (1847{\cdot}599_5 - 0{\cdot}5_9) \pm (0{\cdot}5_1 \pm 0{\cdot}0_5).$$

This discussion leaves open the possibility that the $1847{\cdot}599_5$ may be as much as 1 too large, but gives no reason for expecting this to be the case.

§ 8. THE EXPANDING UNIVERSE

It is only necessary to mention very briefly the numerical test of equation (3), as this has been dealt with by Sir Arthur Eddington himself in his Presidential Address to the Physical Society*.

Sir Arthur concludes, from the observed recession of the spiral nebulae, that the universe is of the Lemaître type, and, further, that it had at one time a stationary radius given by equation (3). At that stage the universe would have been of the Einstein form, its mass and radius being related by the equation

$$(\text{Total mass})\ G/c^2 = \tfrac{1}{2}\pi R,$$

where the total mass is approximately $N.M_P$.

According to Lemaître's theory, the rate of recession of the spiral nebulae per unit distance, uncorrected for any opposing gravitational effect, is given by the expression $c/R\sqrt{3}$. From these three equations Sir Arthur deduces the prediction for the rate of recession of the spiral nebulae:

528 km./sec. per megaparsec,

in good agreement with the experimental estimates, which range from about 430 to 550 in the same units.

§ 9. SOME CONSEQUENCES OF THE THEORIES

Having seen that Eddington's four predictions are in very good agreement with experiment, and that, in particular, his $hc/2\pi e^2 = 137$ is probably exactly correct, we may consider briefly some of the consequences of the theories. Whenever a new relationship is established between universal constants in physics, we can express the less accurately known in terms of the more accurately known and increase the precision of physical knowledge. In the table (p. 381) two sets of estimates are compared with those obtained using equation (1), which can be assumed with confidence, and with the values obtained when both equation (1) and (2) are assumed.

Millikan's determination of the electronic charge appears to be as accurate as he claimed it to be, but actually somewhat smaller than the true value.

Most of the determinations of e by the crystal and ruled-grating method appear to be definitely too large: and we may presume that the error has been correctly attributed to the mosaic structure that, according to Zwickey, occurs in crystals.

The lower or "spectroscopic" estimate of e/m seems to be quite definitely in error. It is not possible to decide whether the presumed error is experimental, or whether it is due to slight errors in the particular theories on which it is based.

The relationship involving G which was suggested by Fürth†, and which I formerly believed to be of significance, appears to be incorrect. Firstly, it was not in quite as good accord with experiment as might have been expected if it were valid; and the full account of Heyl's‡ recent determinations of G makes

* *Proc. Phys. Soc.* **44**, 1 (1932).

† *loc. cit.*

‡ *Bureau of Standards J. of Research*, **5**, 1243 (1930).

the agreement even less satisfactory. Secondly, in my previous work I found that Fürth's theory for M_P/m disagreed with experiment, and this throws doubt on the rest of his work. Finally, if Fürth's theory involving G were correct, and if Eddington's theories were true or at the most only subject to correction terms, then it would be possible to give a comparatively simple mathematical expression for the number of protons in the universe! It appears to be quite unlikely that the total number of protons in the universe is exactly expressible in a simple way, and hence the confirmation of Eddington's theory by experiment necessitates the abandonment of Fürth's theory.

Table 1. Values of universal constants.

	Birge (1929)	Not assuming equations (1) and (2)	Assuming equation (1)	Assuming equations (1) and (2)
$hc/2\pi e^2$	$137{\cdot}29 \pm 0{\cdot}11$	$137{\cdot}05_9 \pm 0{\cdot}05_4$	137	137
M_P/m	$1838_{\cdot 26} \pm 1$ $1846_{\cdot 61} \pm 2$	$1845_{\cdot 3} \pm 1{\cdot}3$	$1847{\cdot}0_0 \pm 0{\cdot}5_1$	$1847{\cdot}599_5$
$(e/m) \times 10^{-7}$ abs. e.m.u.	$1{\cdot}761 \pm 0{\cdot}001$ $1{\cdot}769 \pm 0{\cdot}002$	$1{\cdot}767_3 \pm 0{\cdot}001_3$	$1{\cdot}7694 \pm 0{\cdot}0004_9$	$1{\cdot}7699 \pm 0{\cdot}0001$
$e \times 10^{10}$ abs. e.s.u.	$4{\cdot}770 \pm 0{\cdot}005$	$4{\cdot}776_4 \pm 0{\cdot}002_5$	$4{\cdot}778_4 \pm 0{\cdot}001_2$	$4{\cdot}7768 \pm 0{\cdot}0004$
$h \times 10^{27}$ erg.-sec.	$6{\cdot}547 \pm 0{\cdot}008$	$6{\cdot}553_5 \pm 0{\cdot}004_7$	$6{\cdot}555_9 \pm 0{\cdot}003_4$	$6{\cdot}551_7 \pm 0{\cdot}001_0$

The acceptance of Eddington's treatment of the expanding universe indicates that the universe has passed through, or started from, a stationary state of minimum size. It is pleasing to find a theory of relativity which distinguishes so markedly between past and future! If the spiral nebulae are now some fifteen or so times as far apart as when packed in the stationary state (the reckoning being relative to atomic sizes which may be used to define an unchanging length) it appears that a period of the order 10^{10} years or more has elapsed since the closest packing. This interval of time is so near the estimates of the age of our own universe that it seems likely that the two periods will be identified. It is interesting to notice that, according to Eddington, the properties of cosmic or penetrating radiation cannot be used to predict directly the types of atomic change that gave rise to the rays. He points out that the light would have been reddened by age, relative to our standards, and might give a means of estimating the interval that has elapsed since the universe was of the stationary or Einstein form.

DISCUSSION

Sir A. S. Eddington said that he was naturally much interested in the paper. All the constants involved were known with sufficient precision except e/m, and the question in dispute was between the high and the low experimental value of this quantity. It was to be noted that the higher value agrees with both of the theoretical figures 137 and 1847·6, while the lower value is at variance with both. The speaker had hoped that his theory would give the number of protons in the universe—a result which the author seemed to consider improbable—but unfortunately it had failed to do so. Not much importance could be attached to the prediction of the age of the universe (10^{10} years) since there was at present available a choice between widely varying estimates.

Dr F. J. W. Whipple. Whilst the reasoning by which Sir Arthur Eddington succeeded in evaluating these natural constants is beyond the comprehension of most of us, I think we may, with advantage, dwell on the way in which two little pieces of algebra have found an application in physics. These are the investigation of the number of homogeneous products of known degree of so many variables and the discovery of an equation the roots of which are the ratios of the roots of a given equation.

We have ${}_{16}H_2 = \frac{1}{2} \cdot 16 \times 17 = 136$ and by adding unity (this seems rather arbitrary; may we say "and one for his nob"?) we get 137, the first of the mystic numbers, the number which determines how the scale of wave-lengths is related to the circumferences of electronic orbits.

Further if ρ be the ratio of the roots of the equation, $x^2 - bx + c = 0$, then ρ satisfies the equation $\rho + 2 + 1/\rho = b^2/c$. If $b = {}_{16}H_2 = 136$ and $c = {}_4H_2 = 10$ then $\rho + 2 + 1/\rho = 1849{\cdot}6$. The two roots of this equation are, we are told, the ratio of the masses of proton and electron and the reciprocal ratios. To a sufficiently close approximation $\rho = 1847{\cdot}6$; this approximation is obtained by ignoring the term $1/\rho$ in the foregoing equation. Taking account of that term we get the approximation quoted in the paper, $\rho = 1847{\cdot}5995$.

Mr Rollo Appleyard, referring to the author's remark that Faraday and Joule had sought the unification of all natural phenomena, said that Oersted before their time had devoted much thought to the same problem.

Author's reply. Sir Arthur Eddington points out that the higher experimental estimate of e/m agrees with both the theoretical figures 137 and 1847·6, whereas the lower estimate does not agree with either. I would emphasize that, without the assumption of *any* experimental estimate of e/m, it can be shown that the other experimental data and the two theoretical figures (137 and 1847·6) are in extremely close mutual agreement.

A VACUUM CALORIMETER FOR HIGH TEMPERATURES

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Received December 24, 1931. *Read and discussed March* 4, 1932

ABSTRACT. A form of the platinum-thermometer type of vacuum calorimeter has been developed which is suitable for the determination of true specific heats at high temperatures, since it is constructed without any organic insulating materials. The design is novel in that the heat is transferred from the platinum coil to the calorimeter by radiation.

The general principles of vacuum calorimetry are discussed and applied to the design of the present calorimeter, and a full description of the constructional details and experimental procedure is given.

§ 1. INTRODUCTION

The vacuum calorimeter was originally developed by Nernst and his collaborators, and in their hands attained to great precision as a means of investigating the thermal properties of matter at low temperatures. As designed by them it was restricted in its range on the high-temperature side by the limitations imposed by organic insulating material and by uncertainty as to the heat-loss by radiation, which increases very rapidly with increase of temperature.

With regard to high-temperature calorimetry, mention must be made of the extremely accurate work of Magnus who uses the method of mixtures. The heated substance is dropped into an aneroid calorimeter of solid copper, of which the rise of temperature is measured. While this method can be used up to very high temperatures, it yields, in the first instance, mean heat-capacities over a large temperature range. From this the curve of heat-capacity as a function of temperature can be constructed, and, by differentiation, the true specific heat at a given temperature can be deduced. The method requires, however, that the slope of the heat-capacity/temperature curve should be accurately known at every point. Also, since the substance is necessarily rapidly cooled from a high temperature to air temperature, it cannot be completely annealed.

Recently two attempts have been made to use the vacuum calorimeter, in which true specific heats of well annealed substances over a small range of temperature are measured, for work at high temperatures. The first of these was due to Sucksmith and Potter*, who measured the true specific heat of nickel over the range 20° to 410° C. They do not claim any great precision, however, for their calorimeter, which was in fact intended mainly to give information as to the shape of the specific heat/temperature curve of nickel in the neighbourhood of its Curie point. The other and more recent adaptation of the vacuum calorimeter for high temperature work was made by Klinkhardt†, who adopted the ingenious plan of supplying the

* *Proc. R.S.* A, **112**, 157 (1926). † *Ann. d. Phys.* **84**, 167 (1927).

measured quantity of heat to the calorimeter by bombarding it at a known voltage with electrons from a hot filament. The precision of his results is rather low, however; even at temperatures below 500° C. individual values of the specific heat as experimentally determined differ from the mean curve by as much as 3 per cent in some cases. Also, his measurements of thermal capacity were made over temperature ranges of about 4° C., which are inconveniently large when investigations are being made in the neighbourhood of a transition point. The method could, no doubt, be developed further, and rendered more accurate.

As we wished to make a precise and detailed study of the atomic heats of elements in both the solid and liquid phases and especially in the neighbourhood of their melting points, an extensive series of experiments has been carried out to explore the possibilities of other methods of design for high temperatures*. The design finally adopted is very satisfactory and, so far as we know, novel, in that the heat supplied to the calorimeter from the heating coil, which also serves as a platinum thermometer, is transferred by radiation instead of by solid conduction, the advantage being that the coil, while perfectly insulated from the calorimeter electrically, nevertheless quickly comes into thermal equilibrium with it when the heating current is cut off. The calorimeter, when working over a temperature interval of only 1° C., will determine thermal capacities correct to within 1 per cent.

§ 2. GENERAL PRINCIPLES OF VACUUM CALORIMETRY

In order to make an accurate determination of heat-capacity by means of the vacuum calorimeter, it is necessary to know the amount of heat supplied electrically to the calorimeter, and the resulting rise of temperature. If it is desired to experiment on a substance in the liquid as well as in the solid phase, the heat-capacity of the necessary container must be determined separately.

We shall deal here only with the particular type of calorimeter in which the heat is supplied by means of a coil of platinum wire, the same coil serving as a resistance thermometer to measure the resulting rise of temperature.

The energy supplied is usually deduced from a knowledge of the time-integral of the watts developed in the coil during the time of input, which we will call t_i. This measurement presents no difficulty, provided that accurate ammeters and voltmeters are available and that t_i is not made unduly small. The question where this energy input is developed requires some consideration, as connexion to the platinum coil is necessarily made through leads. If these leads are of low electrical resistance, so that the wattage in them is negligible, then their thermal resistance is also very low and the heat-leak from the calorimeter is large. It is best, of course, to make the resistance of the coil so large that the thermal resistance of the leads may be adequate, and yet their electrical resistance small compared with that of

* We wish to acknowledge here the work done by Mr L. G. Stoodley who made some preliminary investigations.

the coil. There is, however, a limit in practice to the possible resistance of the coil, set by the maximum resistance which can be measured with the bridge available*. The matter is considered further in § 5.

The measurement of the rise of temperature produced by the heating-current is intimately connected with the question of correction for heat-loss. For the sake of simplicity we will assume that before the current is switched on the calorimeter and its surroundings are at the same temperature, which is maintained constant by a thermostat. The measurement of the initial temperature with the coil, used as a platinum thermometer, involves no difficulty. After this measurement has been made, the heating-current is switched on for the time t_i and a certain known amount of heat is supplied to the calorimeter. On switching off, however, the coil is found to be hotter than the calorimeter by an amount depending on the heating-current and on the design. Also the temperature inside the calorimeter is not uniform on account of the finite thermal conductivity of container and its contents. Before making any temperature measurements, it is therefore necessary to wait for a certain length of time, t_e, for thermal equilibrium to be re-established. During this time, however, heat is being lost by the calorimeter, so that, when the final temperature is actually measured it is lower than that corresponding to the energy input. Also heat is lost by the calorimeter during the time of input t_i. This heat loss is due to radiation from the calorimeter surface, to gaseous conduction, and to solid conduction along the leads and suspensions of the calorimeter. Its total magnitude can be reduced by suitable design, but it can never be made so small as to be neglected altogether, at any rate at high temperature where radiation is considerable. A correction is therefore necessary. t_e

In order to make the correction small, the calorimeter must be designed so that the heat lost by the calorimeter during $(t_i + t_e)$ shall be small compared with that imparted to it during t_i.

Let A be the area of the emitting surface of the calorimeter, A

E the effective emissivity of this surface, assuming, for the purpose of calculation, that all the heat is lost from the surface and none by solid conduction up the suspensions and leads†; E

C_c the thermal capacity of the calorimeter; and C_c

β the rise in temperature of the calorimeter as a whole produced by the heating current during the time t_i. β

For the purpose of design we shall assume that, during the time t_e before thermal equilibrium is established between the coil and the calorimeter, the temperature-excess of the calorimeter above its surroundings does not differ much

* In our case, for instance, a Callendar-Griffiths bridge is used which is of course very convenient for platinum thermometry, but the maximum resistance which this particular instrument will measure is 50Ω.

† The justification of this procedure, which is admittedly a rough approximation, is that for small temperature-differences the total heat-loss due to radiation, and to solid and gaseous conduction depends on a single factor, viz. the temperature-difference between the calorimeter and its surroundings

from β. Actually the temperature will decrease slowly with time, but the difference will not be large in a reasonably well heat-insulated calorimeter. Then

$$\text{heat input during time } t_i = C_c\beta.$$

Now, we can assume that during t_i the calorimeter temperature rises linearly with time. Hence

$$\text{heat lost during } t_i = \tfrac{1}{2}EA\beta t_i.$$

Also

$$\text{heat lost during } t_e = EA\beta t_e.$$

Therefore

$$\frac{\text{heat lost during } (t_i + t_e)}{\text{heat gained during } t_i} = \frac{EA\beta\,(\frac{1}{2}t_i + t_e)}{\beta C_c}$$
$$= EA\,(\tfrac{1}{2}t_i + t_e)/C_c. \qquad \text{.....(1).}$$

Assuming that E is made as low as possible by radiation shields, good vacuum, and leads and suspensions of high thermal resistance, this means that the product of A/C_c and $(\frac{1}{2}t_i + t_e)$ should be as small as possible.

Assuming for a moment that C_c is fixed, the ratio A/C_c is of course a minimum for a calorimeter of spherical form. For constructional reasons, however, this form is not convenient, and hence the calorimeter generally approximates in practice a cylinder whose diameter is equal to its height. This, however, merely settles the proportions of the calorimeter, assuming a given value of C_c. The question of what is the best value of C_c remains open. W. P. White* has pointed out that if t is the time taken for the attainment of a given degree of temperature-uniformity throughout the volume of the calorimeter, then t will vary as the square of the linear dimensions of the calorimeter. A is, of course, proportional to the square of the linear dimensions and C_c to the cube. Hence it seems that At/C_c is proportional to the first power of the linear dimensions, so that the calorimeter should be as small as possible. This argument, however, is not applicable if t is governed not only by the time taken for the heat to diffuse through the calorimeter but also by the time taken for the coil to re-attain thermal equilibrium with the calorimeter, after the heating current has been switched off.

This latter time is fixed by the properties of the coil and by its thermal contact with the calorimeter, rather than by the dimensions of the calorimeter. Further, White's argument is not necessarily applicable in determining the accuracy of determination of the heat-capacity of the contents of a calorimeter as opposed to the heat-capacity of calorimeter and contents together. If the calorimeter is too small, its thermal capacity may become large compared with that of its contents, in which case the determination of the heat-capacity of the contents will be subject to large errors. Hence, although we can say quite generally that the calorimeter, if cylindrical, should have the proportions mentioned above, we cannot state the conditions that $(A/C_c)\,(\frac{1}{2}\,t_i + t_e)$ should be a minimum without reference to the particular type of construction contemplated. We shall explain later how we solved the problem in our particular case.

* *J. Amer. Chem. Soc.* **40**, 1894 (1918).

The thermal requirements of the design having been stated the electrical requirements must next be considered. This involves deciding what is the largest resistance which the bridge available will measure, and the highest temperature at which it is desired to work. These two data fix the upper limit to R_0, the resistance of the platinum coil at 0° C. The next consideration is the percentage accuracy required in the determination of the temperature-rise. Having settled this, and knowing the possible experimental error of a bridge-balance, we arrive at a minimum permissible value for the increase in the resistance of the platinum coil due to rise in temperature of the calorimeter, which can be measured with the required accuracy.

R_0,

If the calorimeter is to be used for examining in detail the variation of heat-capacity with temperature, the rise of temperature of the calorimeter corresponding to the heat imparted during time t_i (which we shall denote by β) must not exceed a definite amount, or the fine detail of the variation of heat-capacity with temperature will be lost.

β

Let α be the temperature-coefficient of the platinum coil. Then we have

α

$$R_0 \not> \text{a definite value} \qquad \ldots\ldots(2),$$

$$R_0\alpha\beta \not< \text{a definite value}^* \qquad \ldots\ldots(3),$$

$$\beta \not> \text{a definite value} \qquad \ldots\ldots(4).$$

Also, if R_l is the resistance of the leads, the restriction that the watts developed in the leads shall be a small fraction of the total wattage imposes the further condition

R_l

$$R_0 \gg R_l \qquad \ldots\ldots(5).$$

A compromise between all these requirements will lead to the choice of a definite value for R_0 and give a guide as to the value of β, though this latter quantity will no doubt vary somewhat from experiment to experiment.

We have now indicated the method of arriving at the most suitable electrical resistance for the calorimeter and have formulated the thermal requirement that $A\,(\frac{1}{2}t_i + t_e)/C_c$ should be a minimum. So far the discussion has been quite general, but in order to carry it further we must describe the particular method of construction which we found best for high-temperature work.

§ 3. PRINCIPLES OF DESIGN OF PRESENT CALORIMETER

The difficulty of constructing a vacuum calorimeter for high temperatures largely consists in reconciling the two opposing requirements that the coil should have high electrical insulation (if the platinum thermometry is to be really reliable) and yet good thermal contact with the calorimeter (if t_e is to be reasonably small).

After considerable experiment, we have concluded that the best method of

* If it is desired that the increase in resistance due to the temperature-rise shall be measurable by moving the slider over the bridge wire without changing the bridge coils, there is a further condition

$$R_0\alpha\beta \not> \text{a definite value} \qquad \ldots\ldots(3a).$$

construction is to insulate the coil from the calorimeter and allow the heat-transfer from coil to calorimeter to take place by radiation. The arrangement adopted is shown, purely diagrammatically, in figure 1.

A is the calorimeter round which is wound a coil *B* of blackened platinum, well insulated from it. This coil radiates to the surface of the calorimeter, which is blackened, and to the inner surface (also blackened) of the silver shield *C* which is in good thermal contact with the calorimeter. The blackening is shown in the figure by thick lines. *D* is an outer silver radiation-shield, which also makes good thermal contact with the calorimeter.

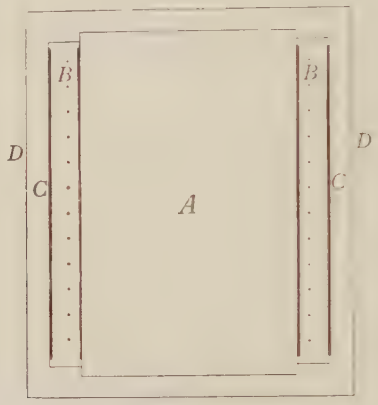


Fig. 1.

The theory of this method of design, showing, in particular, how t_c can be approximately calculated, is as follows: First assume that both the resistance R_0 and the gauge of the wire have already been settled. This latter quantity is generally fixed by mechanical rather than theoretical considerations, though a theoretical treatment has been worked out. R_0 is of course decided by using the conditions contained in equations (2), (3), (4) and (5). The two most important thermal characteristics of the coil are (i) the maximum temperature excess above the rest of the calorimeter to which it will attain with a given current flowing through it, and (ii) its time constant, i.e. the time taken for this temperature excess to diminish to e^{-1} of its original value, when no current is flowing.

We shall assume in our calculations that the heat-transfer from coil to calorimeter is entirely by radiation, gaseous and solid conduction being negligible. With the present method of design this is approximately true, at any rate at high temperatures, with which we are principally concerned.

According to the Stefan-Boltzmann law, the flux of radiant energy in
ϕ calories/cm^2-sec. given out by a surface at a temperature ϕ° absolute is

F $$F = B\phi^4 \qquad \text{.....(6),}$$

B where B is a constant which, for a perfectly black body, has the value of

$1{\cdot}36 \times 10^{-12}$*. It follows that the rate of net loss of heat ΔF when the surface is at a temperature excess $\Delta\phi$ above its surroundings (also assumed to be perfectly black) is

$$\Delta F = 4B\phi^3\,\Delta\phi \qquad \text{.....(7).}$$

Hence, provided that $\Delta\phi$ is small compared with ϕ, ΔF is proportional to the first power of the temperature-excess.

We may therefore write

$$\text{loss of heat} = K\theta \text{ cal./cm}^2\text{-sec.} \qquad \text{.....(8),}$$

where θ is the temperature excess, and K is a constant which is proportional to ϕ^3. K

Let r be the radius of platinum wire which forms the coil; r

θ the temperature-excess of the coil above the calorimeter; θ

R_1 the resistance per unit length of the coil at the particular temperature considered; R_1

l the length of the coil; l

ρ the density of material of the coil; ρ

σ the specific heat of material of the coil; σ

J the ratio of the calorie to the watt-second; J

I the current through the coil. I

We shall further assume that the time-constant of the coil is small compared with t_i, which is the case in practice. Now, when the heating-current is switched on, the temperature of the coil will rise very rapidly for a few seconds and then become nearly stationary, subsequently rising slowly at the same rate as its immediate environment, i.e. the calorimeter. If we denote by θ_0 the maximum temperature-excess of the coil, we have θ_0

$$2\pi rK\theta_0 = I^2R_1/J \qquad \text{.....(9).}$$

Equating the rate of loss of heat due to emissivity to the rate of loss of heat as calculated from its thermal capacity and rate of fall of temperature, we have

$$\pi r^2\rho\sigma\,.\,d\theta/dt = -\,2\pi rK\theta \qquad \text{.....(10).}$$

From which the time-constant T is given by T

$$T = r\rho\sigma/2K \qquad \text{.....(11),}$$

and

$$\theta = \theta_0\, e^{-t/T} \qquad \text{.....(12).}$$

It is of course evident, that, in theory, complete thermal equilibrium between coil and calorimeter is attained only after an infinite time. In practice, however, one considers thermal equilibrium to have been reached when the temperature excess falls to an assigned small value, say θ_e. We will denote the corresponding time by θ_e t_e. Then

$$t_e = T\,(\log\theta_0 - \log\theta_e) \qquad \text{.....(13).}$$

* As a matter of fact for some metals the power of ϕ is more nearly the fifth than the fourth. This does not, however, invalidate the linearity of the relation between heat-loss and temperature-excess for small values of temperature-excess.

In deriving this relation we have assumed the wire to be of circular cross-section, although actually it would be better to make it in the form of a flat ribbon, in which the ratio of radiating area to thermal capacity would be greater. This has not been done in the present calorimeter, though future instruments will probably be so wound.

In order to use (13)* to calculate t_ϵ it is necessary to know θ_0 and θ_ϵ. T is of course fixed by the gauge and physical properties of the platinum wire. θ_0 depends on I which is determined by the fact that the rise of temperature β is to be brought about by the energy supplied during the time of input t_i. Let us assume for the moment that the values of β and t_i have been fixed; θ_0 is then known. θ_ϵ is decided by saying that the wire shall be considered to be in thermal equilibrium with the calorimeter as soon as θ_ϵ/β falls to a specified small value. If, for instance, β is 1° C., which is the order of magnitude usual in these experiments, and if we put θ_ϵ/β equal to $\frac{1}{400}$, the error introduced into the measured heat-capacity will not exceed $\frac{1}{4}$ per cent.

When the present calorimeter is used for work on metals, t_ϵ, the time for the coil to come into thermal equilibrium with the calorimeter, is of a much larger order than the time required for the heat supplied to the surface of the calorimeter to diffuse uniformly through it. Hence the condition, mentioned in the previous section, that the calorimeter should be as small as possible, does not apply in this case, and indeed the question of size is decided by the requirement that the heat-capacity of the calorimeter should be small compared with the heat-capacity of its contents. The matter presents no difficulty in practice.

The requirement that $(A_1'C_c)(\frac{1}{2}t_i - t_\epsilon)$ shall be a minimum then reduces to requiring that $(\frac{1}{2}t_i + t_\epsilon)$ shall be a minimum. The problem may be stated as follows: We have a calorimeter with a given thermal capacity C_c wound with a coil of given length, gauge, and radiation characteristics, and we intend to use it in an experiment in which the rise of temperature is β. It has already been decided that the final temperature shall be measured at the time when θ has fallen to a certain predeter-
p mined fraction of β, say $p\beta$. During the time $(t_i + t_\epsilon)$, however, heat will be lost by radiation, and a correction must be made. It is known that this correction, expressed as a percentage of the total heat-input during t_i, is proportional to $(\frac{1}{2}t_i + t_\epsilon)$. What is the best value of heating-current to choose so that this percentage correction shall be a minimum?

Now, the product of the thermal capacity and the rise in temperature during input must be equal to the heat supplied during t_i.

Hence $$\beta C_c = I^2 R_1 l t_i / J \qquad \text{.....(14).}$$

Also from (9) $$\theta_0 = I^2 R_1 / 2\pi r K J.$$

Substituting in (14) we get

$$\theta_0 = \beta C_c / 2\pi r l K t_i.$$

* It must be understood that equation (13) is used merely as a guide for design purposes. In actual use of the calorimeter t_ϵ is determined experimentally.

Hence from (13)

$$\tfrac{1}{2}t_i + t_e = \tfrac{1}{2}t_i + T\left(\log \frac{\beta C_c}{2\pi r l K t_i} - \log \theta_e\right)$$

$$= \tfrac{1}{2}t_i + T \log \frac{C_c}{2\pi r l K t_i p} \qquad \text{.....(15).}$$

Differentiating, one finds that $(\frac{1}{2}t_i + t_e)$ is a minimum, when

$$t_i = 2T \qquad \text{.....(16).}$$

This means that, during the input period of an experiment, a voltage must be applied to the coil such that the required temperature-rise β is produced during a time equal to twice the time-constant of the coil.

At first sight it might appear that the present method of construction, in which the heat is transferred from coil to calorimeter by radiation alone, would be useless for work at lower temperatures, since by equation (7) K is proportional to the cube of the absolute temperature, and hence at lower temperatures T and t_e will become very large. On the other hand, it must be remembered that if gaseous conduction and heat-leakage along the leads and suspensions are so low that radiation is the predominant factor in heat-transfer, then E of equation (1) will be affected by temperature in the same way as K of equation (8) and hence the correction for heat-loss during $(t_i + t_e)$ will tend to be at all temperatures about the same fraction of the total input.

§ 4. CONSTRUCTION OF PRESENT CALORIMETER

An upper limit to the dimensions of the calorimeter was imposed mainly by mechanical considerations, since the present form of calorimetry necessitates the enclosure of the calorimeter and certain other apparatus in an evacuated vessel. The vessel here used consists of a pyrex glass tube sealed at one end, and connected to a pump system to be subsequently described. The diameter of the tube, 80 mm., approaches the limits set by the adaptability of glass as a material for constructing apparatus of this type, though the use of metal would, no doubt, permit the adoption of larger dimensions.

The above consideration led to the requirement that the external diameter of the calorimeter should not exceed 60 mm. overall. The winding of the platinum wire coil and the fixing of a radiation-shield of silver foil permitted a diameter of not more than 50 mm. for the actual container of the substance under investigation. This container A, figure 2, consists of a hollow cylinder of mild steel, 50 mm. in diameter by 80 mm. long, turned from a solid rod to a wall thickness of about 0·5 mm. It was constructed with a screw-on lid B, of diameter equal to that of the cylinder, and a neck 6 mm. high by 15 mm. in diameter, closed by a screw-cap C, the former being purely for constructional reasons, the latter for the purpose of filling. In order to simplify certain silver-soldering operations in later stages of the construction, the whole steel container was nickel-plated to a thickness of about 0·05 mm.

It has been pointed out that, for the efficient working of a vacuum calorimeter, the platinum coil must quickly take up the temperature of the calorimeter, and it is therefore desirable in the case where the transfer of heat is by radiation that the coil should be completely enclosed in surroundings which are in good thermal contact with the main bulk of the calorimeter. To this end, the coil which consists of 370 cm. of 38-s.w.g. platinum wire was wound bifilarly in the annular space between the steel container and a case of silver foil 0·1 mm. thick, *D* in figure 2. Thermal contact between this case and the container is effected by means of sixteen 10-B.A. cheese-headed steel screws *E*, which were silver-soldered head downwards to the container, the silver-foil case being held down firmly with nuts.

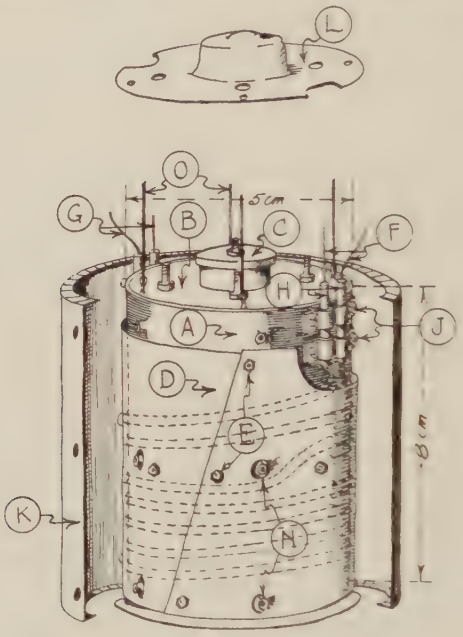


Fig. 2.

The outside of the steel container, the inside of the silver case, and the platinum wire were blackened by coating with Bakelite* varnish, which was carbonized by baking in a furnace at about 350° C. To remove any comparatively volatile substances that might still be present, a further baking was given in vacuo at 400° C. Tests show that the emissivity of the surface thus obtained approaches that of a full radiator, and also that the blackening withstands prolonged heating in vacuo at a dull red without deterioration. Moreover, the high-temperature coefficient of resistance which is characteristic of pure platinum was obtained when the coil was calibrated as a thermometer, which indicates that the blackening on the wire does not impair its quality as a resistance thermometer.

* We have no doubt that other varnishes would be equally satisfactory, and we have, in fact, tested a stove enamel sold under the name of "Namo" (heat-resisting grade) and find it quite suitable.

Electrical contact of the coil with either D or A was prevented by the interposition of thin sheets of mica, though, as a matter of fact, the presence of this mica unduly increases the time-constant of the coil, and will be avoided in future models. To prevent adjacent turns from touching each other, the wire was wound over six narrow strips of asbestos fabric* about 3 mm. wide, placed longitudinally along the container. The wire embedded itself in this tape, and risk of turns touching was eliminated without undue tension having to be applied to the winding. The ends of the coil were fixed by twisting them round pieces of small quartz capillary slipped over thin iron nails soldered head-down to the case.

The leads F to the coil and the compensating leads G consist of 26-s.w.g. platinum wire. They pass through quartz capillary tubing H, which has been coated with a film of silver by chemical deposition and then silver-plated to a thickness of about 0·25 mm. The space between the platinum and the quartz is filled with alundum cement, grade RA 562, and experiment showed that good thermal contact existed between the wire and silver coating. As it was desirable to make the temperature of the lower ends of the leads the same as that of the main bulk of the calorimeter, the tubes were bolted down to the steel container by means of silver-foil straps and the bolts J. In order that it might be possible to test the insulation of the platinum coil, the compensating leads were connected electrically at the lower end to the container. At 300° C. the insulation resistance between the platinum coil and the container was of the order of 200 MΩ.

Figure 2 shows the top L and the sides K of the radiation-shield partly removed from the calorimeter. The former was bolted down to the lid by 5 bolts, and another radiation-shield was fixed to the bottom of the calorimeter in a similar way. The nuts holding them down were shielded with a wrapping of silver foil. Twelve steel pillars N, 4·5 mm. long and 3 mm. in diameter, tapped through the centre and soldered to the container, served to carry the side shield K. The countersunk heads of the screws holding the shield down to these pillars were coated with silver solder to reduce their emissivity.

The calorimeter was hung up by means of the suspensions O, each consisting of 4 cm. of 26-s.w.g. platinum. Provision was made at the top of each suspension for adjustment in three dimensions in order that it might be possible to make the calorimeter hang symmetrically; and for reasons which will appear later, an insulating link in the form of a glass bead was incorporated in each suspension.

Figure 3 shows the calorimeter with radiation-shield in position hanging from the copper disc P. The latter is 13 mm. thick and machined with a screw thread to fit a corresponding thread in the copper cylinder Q. The purpose of the cylinder Q was to meet the requirement that the whole of the environment of the calorimeter, with which it exchanges heat, should be at a uniform temperature. This was ensured by giving the cylinder the wall-thickness of 3 mm., the bottom being closed by a copper disc covered with silver foil and fixed by four nuts and bolts to the

* This fabric was rendered a very good electrical insulator at high temperatures by boiling it for many hours in distilled water to remove soluble salts, and finally heating it to about 600° C. to remove its cotton content by carbonization and subsequent oxidation.

walls. The inside was electro-plated with silver to reduce radiation exchanges with the calorimeter, while the outside was blackened in order that its temperature might be governed by a thermostatically controlled furnace surrounding the pyrex tube in which the apparatus hangs. The copper disc P was covered with silver foil on both surfaces as it was undesirable to allow it to radiate appreciably to the cooler parts of the apparatus above. Four holes, U, about 1 cm. in diameter drilled in the disc aided the evacuation of the space between the calorimeter and copper

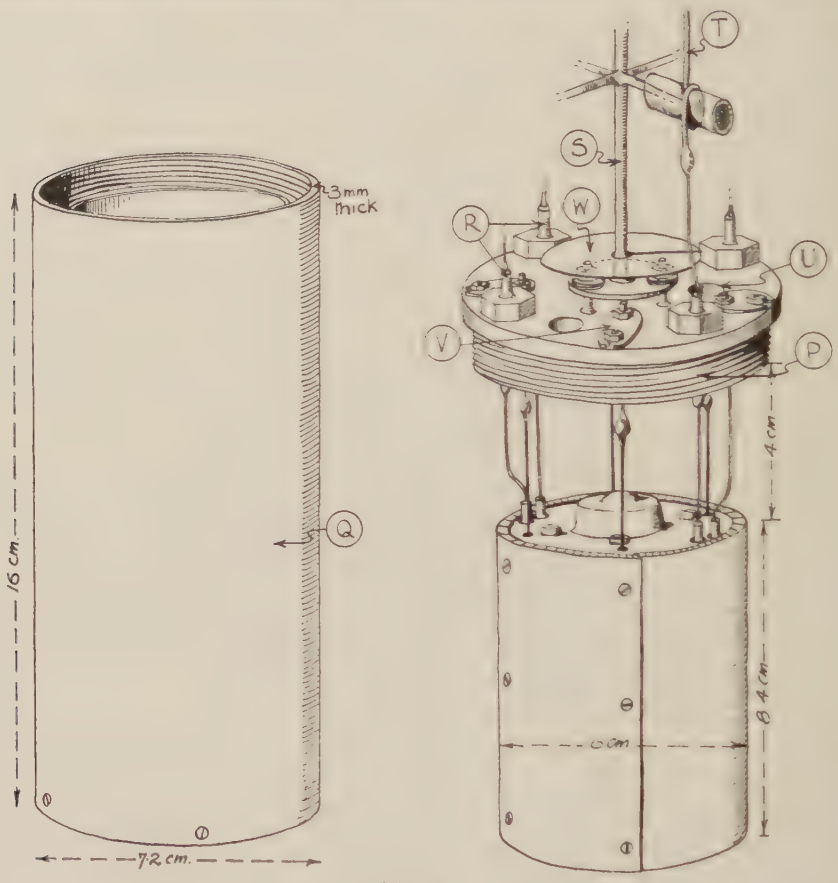


Fig. 3.

cylinder, but silver-foil cowls over them prevented undue increase in the radiation loss. The four leads from the calorimeter were brought through the copper disc by means of four bushings R, serving to insulate them electrically but not thermally. The bushings consisted of silvered quartz tubes which were hard-soldered into holes passing through four copper bolts, which, in their turn, were screwed into the copper disc P. These bolts together with the suspension adjustors, V, were covered with silver-foil shields, which are omitted, however, in the figure.

A steel frame S served to support the apparatus mechanically and also to carry the electrical leads to the top of the vacuum chamber. The lower end of the central

rod terminated in a steel plate which was bolted to the copper disc. To prevent a large thermal leak up the rod, mica was interposed between the metal parts, but a fine copper wire joined the frame and the copper disc electrically. This connexion, in conjunction with the insulating links in the suspensions, made it possible to test whether or not the calorimeter was hanging freely inside the copper cylinder. All that was necessary was to test the insulation between the frame and the compensating leads, since the former was connected to the copper cylinder, and the latter to the main part of the calorimeter. 20-s.w.g. copper wire was used for the leads T, which were insulated from the cross members of the frame S by quartz sheaths. W is a circular radiation shield of silver foil.

The top of the pyrex tube containing the apparatus was closed, with the aid of a wax seal, by a copper cap through which the leads were brought out by insulating glass bushings, wax again being used to effect a vacuum-tight seal. From here the compensating leads were taken to a Callendar-Griffiths bridge capable of measuring resistances up to 51 Ω, and the platinum-coil leads were taken to a two-way mercury-contact switch enabling the coil to be connected either to the bridge for temperature measurements or to an electrical supply for the energy-input. The latter was measured with an ammeter and voltmeter. The remainder of the vacuum apparatus consisted of a two-stage mercury-vapour pump, backed at about 1 mm. of pressure by a piston-type oil pump. As any contamination with mercury of the silver radiation-shields enclosing the calorimeter would have increased their emissivity, a mercury-vapour trap, containing sodium-potassium alloy, was placed between the pump and the main apparatus. A Pirani vacuum gauge near the pyrex tube measured the pressure, vacua of the order of 10^{-3} mm. being attained. A gauge of this type is particularly suitable, since it directly measures that characteristic of the residual gas which is peculiarly relevant, namely its thermal conductivity. Although 10^{-3} mm. is a comparatively poor vacuum, little would be gained by improving it beyond this value when the calorimeter is used at temperatures above 200° C., for at such temperatures the loss of heat by gaseous conduction is but a small fraction of the total.

The furnace surrounding the pyrex tube consisted of a thick-walled copper pipe on which was non-inductively wound 100 Ω of 34-s.w.g. nichrome wire, the electrical and thermal insulation consisting of asbestos paper and asbestos wool respectively.

The time-constant of the winding of the calorimeter calculated from equation (2) comes out to be about 3 sec. at a working temperature of 300° C. However, this equation is only meant to give the order of magnitude of this quantity, and assumes in fact that the coil radiates directly to the environment to whose temperature it is required ultimately to fall, without the interposition of any other material. Experiment showed the actual time-constant to be about four times the calculated value, the discrepancy being due, no doubt, to the mica insulation between the coil and the metal surroundings, to the emissivity of the radiating surfaces being somewhat less than that of a perfectly black body, and to the thermal capacity of the strips of asbestos fabric on which the coil is wound.

For 38-s.w.g. blackened platinum wire at a temperature of 300° C., and a heating current of 200 mA. (which is of the order usually employed), θ_0 as calculated from equation (9) comes out to be 25° C.

The heat-leak from the calorimeter at 300° C. was found experimentally to be about $6{\cdot}5 \times 10^{-3}$ cal./sec.-degree. This was of the same order of magnitude as the value obtained by calculating the leak up the leads, the radiation-loss, and the gas-conduction, the results of Heilman* being used to compute the loss due to radiation, and of Soddy and Berry† that due to gas-conduction.

Assuming all this heat to be lost by the side radiation-shield, the maximum temperature-difference which could exist between the ends of the steel pillars carrying the shield was about $\frac{1}{30}$° C., and the maximum temperature-difference between any two points of the silver shield was about $\frac{1}{20}$° C.

The platinum coil had a resistance at 0° C. of 20·6 Ω. It was calibrated as a thermometer at the ice point, the steam point and the melting point of bismuth. For the latter fixed point a temperature of 271·0° C. was accepted from the results of Adams and Johnston, and Mylius, Grosehuff and Holborn‡. The constants α and δ in Callendar's formulae for platinum thermometry had, within the limits of experimental error, the values usually obtained for platinum of high purity. A change of 1° C., the average amount by which the calorimeter was raised in temperature in a heat-capacity determination, corresponded to a change of resistance equivalent to 8 cm. of bridge wire. The time of heat-input was usually of the order of 200 sec.

Assuming a heat-capacity of 0·35 cal. cm.^{3} (an average value for common metals) the ratio of the thermal capacity of the full calorimeter to the empty calorimeter is about 4 to 1.

§ 5. CALCULATION OF RESULTS

The essential experimental observations necessary for the computation of the heat capacity of the calorimeter are represented graphically in figure 4. The graph (*a*) shows the resistance (and consequently the temperature) of the platinum coil plotted as a function of time; *AB* represents the behaviour of the coil before the heat-input and *CDE* its behaviour after the heating current has been switched off. The portion *CD* corresponds to the state of affairs when the winding is appreciably hotter than the calorimeter, temperature-equilibrium being re-established at *D*. The term "equilibrium" does not mean that the coil and the calorimeter are at the same temperature, as the current required for the bridge-measurements maintains the coil at a somewhat higher temperature than the calorimeter. However, this elevation of temperature is the same for *DE* as for *AB*; thus we can use the curves *AB* and *DE* to deduce the temperature-rise of the calorimeter due to the heat-input, although a correction must be applied to find the mean temperature of the calorimeter during the determination.

* *Trans. Amer. Soc. Mech. E.* **51**, 287 (1929).
† *Proc. R.S.* A, **83**, 254 (1909).
‡ Landolt-Bornstein, *Tables* **1**, 329 (1923).

The dotted lines BF and FD represent the temperature of the main part of the calorimeter (and hence the outer shield) during the periods t_i and t_e respectively. We make the following assumptions, for which justification has been found experimentally: (*a*) The temperature of the calorimeter rises linearly with time during the time interval t_i; and (*b*) the law of cooling for the portions AB and FDE is the exponential law of Newton, according to which both curves are asymptotic to the constant-temperature line GH corresponding to the temperature Δ of the copper cylinder surrounding the calorimeter. Δ

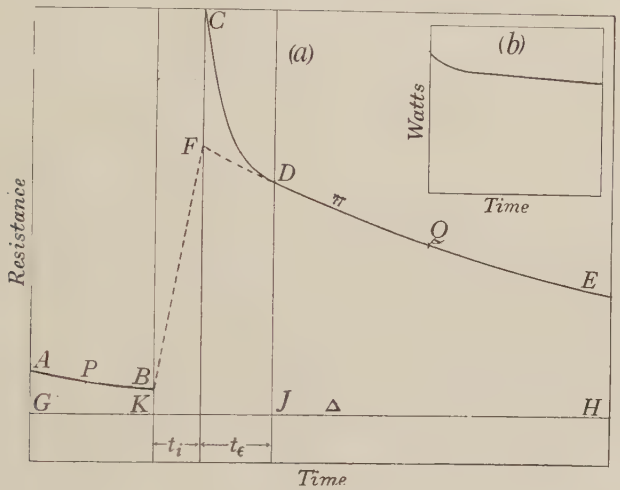


Fig. 4.

These assumptions require the condition, so far as the times t_i and t_e are concerned, that the thermal capacity of the parts of the calorimeter appreciably hotter than the main bulk be small compared with the total heat-capacity, which condition is satisfied in this calorimeter.

Let π be the temperature of the platinum coil, measured from the same zero as Δ. Then π

$$\pi - \Delta = (\pi_0 - \Delta)\, e^{-kt} \qquad \text{.....(17),}$$

Δ and k are found by taking the slopes of the curves at points P and Q well removed from each other in the temperature scale. If S_P and S_Q are these slopes, and the corresponding temperatures are π_P and π_Q respectively, then S

$$S_P = k\,(\pi_P - \Delta)$$

and

$$S_Q = k\,(\pi_Q - \Delta).$$

It follows that

$$k = \frac{S_Q - S_P}{\pi_Q - \pi_P} \qquad \text{.....(18),}$$

and

$$\Delta = \pi_P - S_P \frac{\pi_Q - \pi_P}{S_Q - S_P} \qquad \text{.....(19).}$$

The temperature π_D at D is, on account of the heat lost during the time $t_i + t_e$,

lower than that corresponding to the heat-input by an amount which is given by the product of k and the area $BFDJK$. In practice, the correction for this loss may be divided into two parts, each being calculated algebraically as follows.

The temperature π_F, which the calorimeter would have had if it had lost no heat during t_e is given by

$$\pi_F - \Delta = (\pi_D - \Delta)/e^{-kt_e} \qquad \text{.....(20),}$$

while the correction for the heat-loss during t_i is

$$\tfrac{1}{2}k\,(\pi_B + \pi_F - 2\Delta)\,t_i.$$

Hence the temperature-rise which would have taken place if there had been no heat loss is

$$\pi_F - \pi_B + \tfrac{1}{2}k\,(\pi_B + \pi_F - 2\Delta)\,t_i.$$

To the energy-input, obtained from graph (*b*), figure 4, three corrections are necessary. These are: (*a*) Correction for the fact that while the heating-current is flowing the calorimeter is not receiving the small influx of energy due to the bridge current; (*b*) subtraction from the measured power of the power necessarily liberated in either ammeter or voltmeter; and (*c*) correction for the power liberated in the leads between the measuring instruments and the calorimeter.

The part of the power developed between the instruments and the copper disc is easily computed, and none of it enters the calorimeter; but of the power developed in the platinum leads, between the copper disc and the calorimeter, about half goes into the calorimeter and must, therefore, be reckoned in the energy-input. In the present calorimeter this amounts to about $\frac{1}{4}$ per cent of the total energy-input.

§ 6. CONCLUSION

The design described in this paper is valid up to at least 500° C. and probably higher, though the maximum resistance measurable by the particular bridge used did not allow work above 370° C. on this occasion.

The sum of the greatest errors possible in the measurement of current, voltage and time are estimated at $\frac{1}{2}$ per cent, while those possible in the determination of the temperature-rise, due to inaccuracies in bridge-measurements and the heat-loss correction, do not amount to more than another $\frac{3}{4}$ per cent at the most in the case of the empty calorimeter, where they are likely to be most serious. A series of tests has been made of the heat-capacity of the calorimeter, both empty and full, over a range extending from air temperatures to over 300° C., and the greatest deviation of an individual determination from the mean smooth curve has not exceeded 1 per cent. In order to test the validity of the method of calculating results, determinations were made at the same temperature with varying values of t_i; also, in deducing the temperature-rise, different values of t_e were taken, but no systematic deviation of the final results from the mean curve was found. High accuracy in the determination of the thermal capacity at individual temperatures

is, of course, valueless unless corresponding precision is obtained in measuring the temperatures themselves, but the platinum thermometry is quite adequate for this.

The calorimeter here described is at present being used to investigate the heat-capacities of a series of pure metallic elements at high temperatures.

§ 7. ACKNOWLEDGMENTS

In conclusion, it is a pleasure to express our thanks to Prof. H. Stansfield, in whose laboratory this calorimeter has been developed, for his kind interest and support. We are much indebted to Mr E. E. Mann for kindly drawing figures 2 and 3.

DISCUSSION

Mr J. H. Awbery said that the authors had made a valuable contribution to the equipment of workers engaged on heat problems. He would look forward to seeing the results obtained with various materials.

Mr C. R. Darling asked what method was employed for measuring the temperature of the silver shield, which appeared to be of considerable importance.

Dr Ezer Griffiths. Could the authors give fuller information concerning correction for radiation-loss? Is it assumed that the temperature of the sheet of metal *D*, figure 1, is identical with that of the resistance-thermometer coil? I would suggest that information as to the uniformity of the temperature could be obtained by means of thermo-elements soldered to the surfaces.

Authors' reply. We are grateful to Mr Awbery for his kind remarks about the calorimeter.

With regard to the points raised by Dr Ezer Griffiths and Mr Darling: The temperature of the outer silver shield *D*, figure 1, is assumed to be the same as that of the main part of the calorimeter. The validity of this assumption and of the further one that the temperature of *D* is uniform is supported by the figures for the maximum possible temperature-differences which are quoted in the antepenultimate paragraph of § 4.

The temperature of the main part of the calorimeter during $t_i + t_e$, which is shown dotted in figure 4, is deduced as described in figure 5 of the paper.

A NEW TILTED ELECTROMETER

By HUGH CARMICHAEL, B.Sc., University of Edinburgh

Communicated by Prof. C. G. Barkla, F.R.S., January 15, 1932
Read and discussed March 4, 1932

ABSTRACT. A description is given of the construction and performance of a new electrometer on the principle of the Wilson tilted gold-leaf electrometer. The instrument has a quartz fibre "leaf" which moves in hydrogen to reduce sluggishness. There is complete protection of the instrument from atmospheric disturbance, and considerable simplifications are made in the construction and in the method of adjustment. Typical sensitivities of 3 mm. and 30 mm. fibre movement per volt (linear for 2 mm. and 1 mm respectively) have been obtained, and a reliable eyepiece scale sensitivity of 1000 divisions per volt is within the range of the instrument.

§ 1. INTRODUCTION

The tilted gold-leaf electrometer was devised by C. T. R. Wilson[1]. It has been investigated and redesigned by G. W. C. Kaye[2], who gives a useful account of its behaviour, and many manipulative details.

The instrument depends for its sensitivity on the fact that a hanging gold leaf, maintained at or near zero potential, can be attracted out of the vertical by an inclined high-potential metal plate and can be brought near to a critical unstable state of deflection by adjusting the tilt of the plate, its proximity to the leaf, and the plate potential. Near this unstable state the deflection of the leaf is very sensitive to change in its potential. The sensitivity curve given by Wilson and by Kaye is of the type shown in figure 1 (*a*). The deflection of the leaf is not a linear function of the leaf-potential except approximately for a short range on each side of the point of inflection. It is of course possible so to adjust the electrometer that the position of the leaf when at zero potential corresponds to the point of inflection on the sensitivity curve, figure 1 (*b*). The electrometer then has a linear range for small positive and negative leaf-potentials.

In this paper an account is given of a new electrometer designed with the object of eliminating the disadvantages which have been found in electrometers made in this laboratory from the drawing in Kaye's paper. The disadvantages are:

(i) The case of the instrument is not airtight so that the leaf is liable to erratic movement if atmospheric conditions in the laboratory are not steady.

(ii) The electrometer is not protected from draught and stray heat radiations which disturb the uniformity of the temperature of the case and cause convection in the air inside it, while a protecting box makes adjustment of the instrument troublesome.

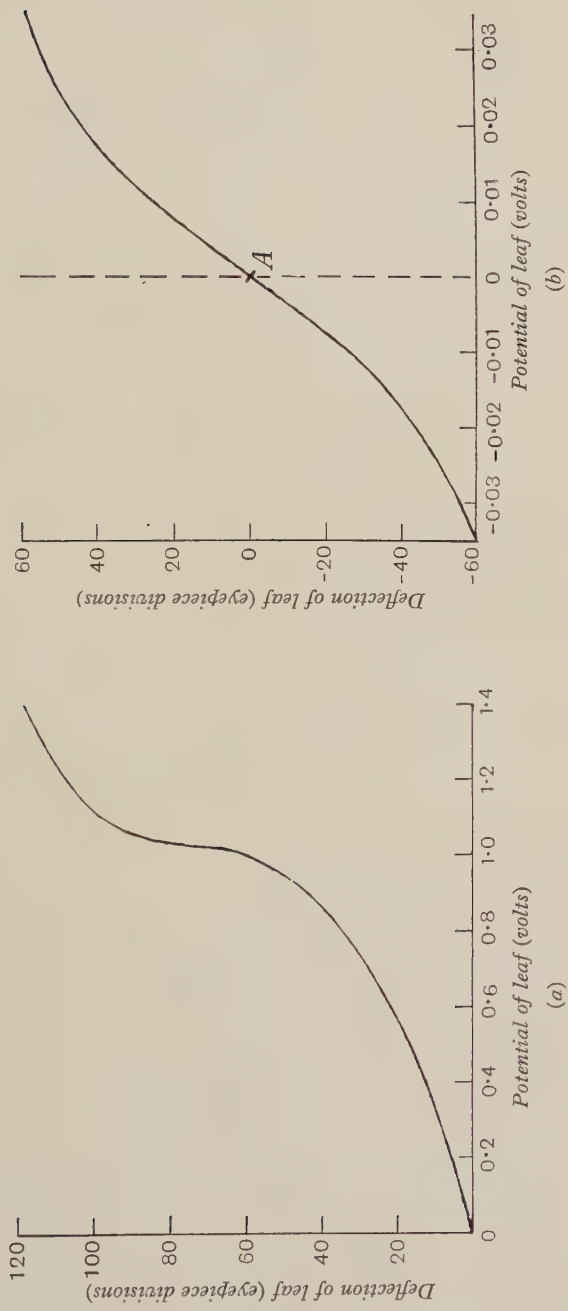


Fig. 1. Typical sensitivity curves.

(iii) The gold leaf itself is not satisfactory, as a sudden or too great deflection often causes a change in its shape which affects the zero reading and the sensitivity. Moreover the leaf is not a good object to focus sharply in the telescope.

(iv) The leaf is sometimes liable to swing out of focus.

(v) At high sensitivity the leaf moves very slowly through the air in the chamber to a new position of rest.

(vi) The instrument is troublesome to adjust and the degree of skill required has always been a serious drawback to its more general use.

These will be referred to by number.

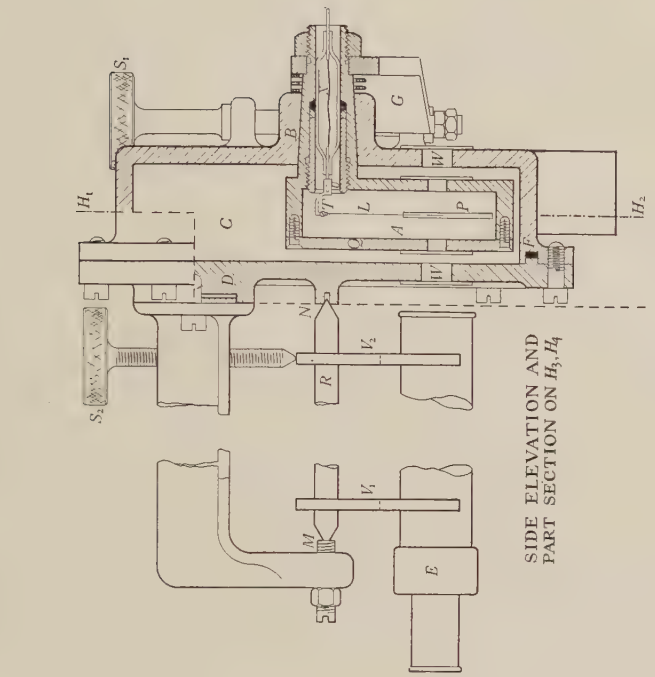
The new instrument is being used as a detector in a null method of comparing the ionizing powers of two X-ray beams. It is connected to an insulated zero-potential electrode which passes into each of two ionization chambers. The cases of the chambers are at approximately equal and opposite saturation potentials, so that the ionization currents due to the beams are in opposite directions with respect to the electrode. They can thus be equalized by cutting down the more powerful beam till the electrometer shows that the common electrode does not change rapidly from zero potential on being disconnected from earth. The rate of leaf-movement is measured for several settings on each side of the true balance point, and the latter found by plotting a rough graph. With the apparatus at present in use, which has a variable aperture controlled by a micrometer screw to cut down one beam, the determination of a balance point may be repeated with an error of less than 0·0001 of the maximum aperture. The electrometer is well suited for making those measurements as it is compact and has an easily varied sensitivity with a high maximum value, a low capacity, and a quick and linear response to small potential changes.

§ 2. DESCRIPTION OF THE ELECTROMETER

The case A, figure 2, of the electrometer is a short circular cylinder with plane ends. It is made of thick brass and is supported by the bearing B inside a larger cylinder C of brass. The bearing B is tapered and ground to fit, and is made gas-tight with tap grease. The front D of the outer case, on which the telescope E is supported, is removable, but when screwed down in position so as to compress the rubber gasket F is gas-tight. The outer case protects the electrometer from non-uniform temperature changes and from changes in atmospheric pressure; cf. (i), (ii) above.

To the outer end of the supporting axle B is fitted a lever G which is moved by a worm screw S_1 and serves to alter the tilt of the electrometer. It is arranged that the point of support of the leaf inside the electrometer is on the axis of the bearing B, so that it is not affected by alteration of the tilt.

The telescope E is clamped on to V blocks V_1, V_2 fixed to a rod R which is supported by bearings M, N on the continuation of the axis of the bearing B. Thus the telescope is always perpendicular to the plane of movement of the leaf, and swings in an arc about the point of suspension of the latter. Movement of the telescope by


SIDE ELEVATION AND PART SECTION ON H_3, H_4
(b)

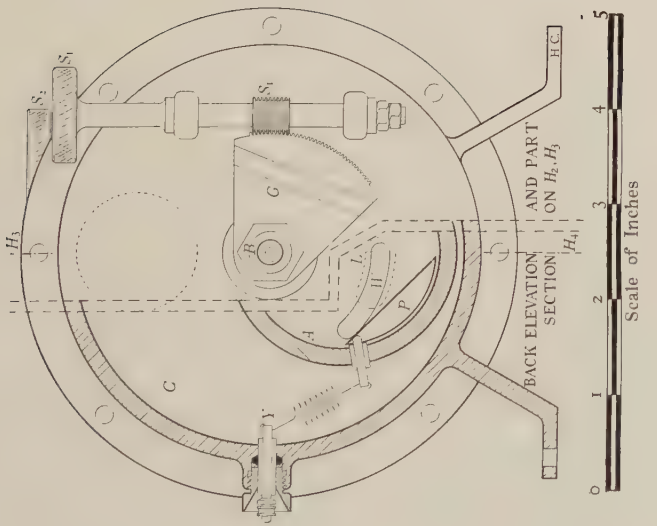

BACK ELEVATION AND PART SECTION ON H_2, H_3
Scale of Inches
(a)

Fig. 2.

a single screw S_2 brings the image of the same part of the leaf on to any eyepiece scale-division, at whatever angle to the vertical the leaf may hang. After the image of the leaf has been focussed on the eyepiece scale in the telescope, the only adjustments—cf. (vi) above—in using the instrument are alteration of (*a*) the tilt by the screw S_1; (*b*) the position of the telescope by the screw S_2; (*c*) the value of the plate voltage.

In the electrometer itself, of which the front Q of the case is removable and not gas-tight, the disposition of the leaf L and the plate P is shown. To insure that the leaf will swing truly—cf. (iv) above—the broad tilted plate of Wilson's electrometer is replaced by a very narrow plate consisting of the straight edge of a piece of thin brass. The field from this edge tends to keep the leaf in the middle of the case. The leaf itself is attached to an electrode T by means of small knife-edged jaws closed by a watchmaker's screw, so that it has a definite hinge. The electrode, which should be as small as possible, passes along the axis of the bearing B to the outside of the electrometer through a quartz insulator X into which it is cemented. A compressed rubber gasket makes a gas-tight holder for the insulator. For convenience in fitting and replacing leaves, the end T of the electrode is removable from the part passing into the insulator. The snap joint U is such that T with the leaf attached may be held in a pair of pincers and pushed into position. The device for varying the distance of the plate from the leaf, provided in Kaye's design, has been dispensed with since, though convenient, it is not essential to the proper working of the electrometer. In its absence a potentiometer for fine adjustment of the plate voltage is necessary.

Narrow windows W cut along the arc of movement of the telescope, and closed with thin glass cemented in position, allow light to pass through the instrument past the leaf to the telescope. A lead from the plate is taken through the outer case on a gas-tight quartz insulator Y. Inlet and outlet taps (not shown in drawing) are fitted for filling the instrument if necessary with a more suitable gas than air (see below). An earthing-key also, on the instrument itself, is convenient. An important feature of the design of this electrometer is the fact that the metal castings are such that they can be worked on a lathe. This greatly simplifies the construction of the instrument.

With a gold leaf approximately 0·5 mm. wide the instrument was found to require a potential of 260 volts on the plate to bring the leaf into the critical state of deflection. The gold leaf however was not very satisfactory and it was decided to replace it by a quartz fibre—cf. (iii) above. A silvered quartz fibre which must be at least as light as a gold leaf 0·25 mm. wide was attached to the electrode by means of a hinge of gold leaf. This fibre was found to form a very satisfactory "leaf" and it provided the additional great advantage that a potential of only 80 volts was required on the plate. This makes for economy and for an increased range of sensitivity. Finally the terminal velocity of the fibre in the gas in the chamber was approximately doubled by using hydrogen instead of air, the viscosity of hydrogen being about half that of air—cf. (v) above.

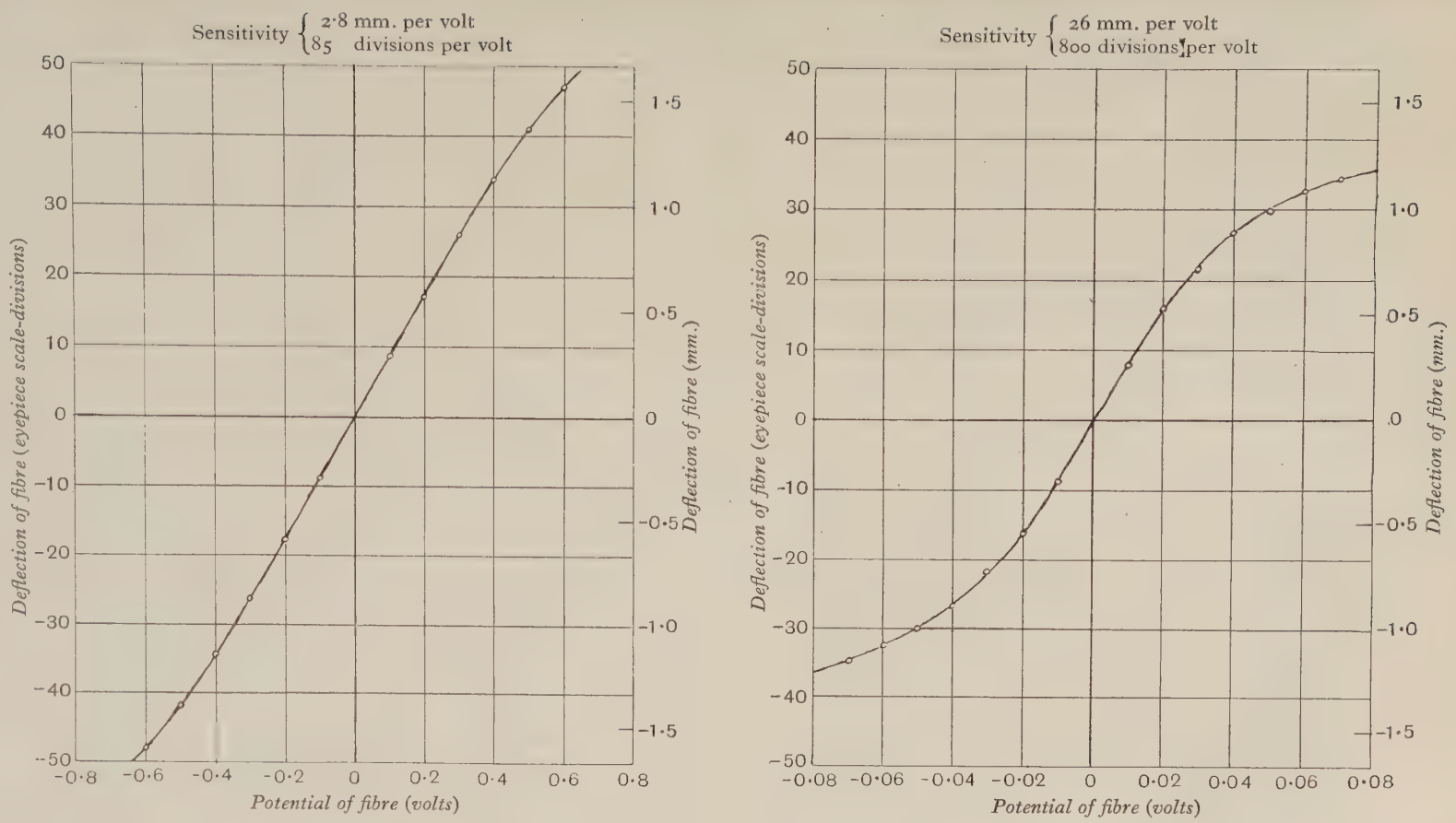


Fig. 3. Calibration curves showing range of linearity at 2·8 and 26 mm./volt.

§ 3. PERFORMANCE

Two typical sensitivity curves are given in figure 3. These give some idea of the range of linearity obtainable with the new electrometer. The magnification is 30 divisions of the eyepiece scale to 1 mm. of fibre movement, about one-half of that used by Kaye.

No erratic movements of the fibre were observed even after handling the outer case, so that the protection of the electrometer is adequate.

The only adverse factor at high sensitivity, given that the plate voltage is constant, is found to be the viscous drag of the gas in the chamber. At a sensitivity of 1000 divisions per volt, with the above magnification, the time taken by the fibre to come to a new position of rest is over 2 minutes, even with hydrogen in the chamber. At less than 500 divisions per volt, however, the response is relatively rapid, and such is the precision of the electrometer that at these sensitivities the magnification may be increased several times.

The gold-leaf hinge does not seem to exert undue control, but it might be possible to replace it by a short cross-piece of quartz attached to the top end of the fibre, with its ends rolling in U supports.

§ 4. ACKNOWLEDGMENTS

The thanks of the writer are due to Prof. Barkla and to Dr R. J. Clark for their help, and to Mr Mollison for undertaking a large part of the construction of the instrument.

REFERENCES

(1) *Proc. Camb. Phil. Soc.* **12**, 135 (1903).
(2) *Proc. Phys. Soc.* **23**, 209 (1911).
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DISCUSSION

Mr S. B. Fulford. I think it would be an advantage if the precise form of the knife-edge jaws which hold the leaf were described. Unless these are very carefully made and adjusted, there is a risk of the gold-leaf hinge becoming cut through, by repeated flexing, particularly if the knife edges are at all opposed. With regard to the excessive damping of the leaf, even when it moves in hydrogen, it might be worth while to modify the design slightly in order to allow the chamber to be evacuated to a moderately low pressure. The performance at high sensitivity would then be much improved, and the damping could be controlled by variation of the pressure.

Mr W. V. MAYNEORD said that he had had some experience of Wilson electrometers used in conjunction with small γ-ray ionization-chambers. He recommended evacuation as a means of getting rid of ionization in the electrometer.

AUTHOR'S reply. By knife-edge jaws I do not mean that the edges are in the least opposed. The leaf is held between the flat surfaces of a slot in the electrode, and the edges of the slot are sharpened so that no metal to which the leaf can easily adhere is left near the hinge. I have of course considered the possibility of reducing the damping of the fibre by evacuating the electrometer. This may be done without modifying the design. Since, however, the viscosity of a gas is independent of the pressure until comparatively low pressures are attained, a pump capable of producing a pressure of at least 10^{-2} mm. of mercury would be necessary. For ordinary uses, since the instrument may be filled with hydrogen by displacement, this would be an expensive complication.

I think that a moderate evacuation, especially of the hydrogen-filled electrometer, would be a very effective method of reducing the ionization due to radiation passing through the electrometer itself.

ON THE SYMMETRICAL MODES OF VIBRATION OF TRUNCATED CONICAL SHELLS; WITH APPLICATIONS TO LOUD-SPEAKER DIAPHRAGMS

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Received January 26, 1932. *Read March* 4, 1932

ABSTRACT. It is shown that in general the stresses in a vibrating conical shell are so complicated that the problem is unsuited to analytical treatment. If the stress were purely extensional, the frequency would be independent of the thickness t and vary inversely as the major radius a. This, however, would necessitate a much larger potential energy at the small end than practice indicates. The expression for the frequency of a shell of constant minor radius is of the form $f = kt^{n_1} a^{-n_2}$ where, for certain conditions, $n_1 = 0{\cdot}22$ and $n_2 = 0{\cdot}67$.

Experimental work with paper, glass and aluminium shells is described. The modes crowd together as compared with the segregation which occurs in the case of a disc. With thick glass or aluminium of comparatively low loss, the nodal frequencies are very clearly-defined peaks. In the case of paper cones driven by coils of small mass, the peaks disappear and the nodal region is indicated by a broad rounded contour. The influence of thickness, apical angle and the mass of the driving coil is considered. Vibrations of the air column within the shell and the general requirements for loud-speaker diaphragms are discussed and illustrated by practical examples.

§ 1. INTRODUCTION

THERE are two salient types of vibration pertaining to truncated conical shells: (*a*) radial modes as in a bell, (*b*) symmetrical modes as in a disc. Radial modes of the shell are associated with bending, whilst the symmetrical modes depend upon bending and extension. This paper deals exclusively with the latter modes, more particularly in their application to loud-speakers of the hornless type, where radial modes are invariably of secondary importance.

So far as the vibrational modes of cylindrical and spherical shells are concerned, one has only to turn to the works of the great applied-mathematicians to find an answer. But the vibrational modes of conical shells are secrets closely guarded from the inquisition of modern analytical methods. This is indeed unfortunate, for although one can obtain an answer empirically in any special case, the apparatus involved is costly and the time vastly in excess of that required for a mere computation. As the matter stands at present, it appears that to establish a general empirical formula embodying the two radii, apical angle, thickness, and Poisson's ratio for various edge conditions, a concentrated or mass attack would be required by a number of investigators. This would undoubtedly be a protracted and laborious process.

The present paper is mainly an account of a number of experiments in this direction, and the general consequences of the results in modern acoustic apparatus.

Although a general empirical formula has not been constructed, the information is adequate to predict the main vibrational frequency band of conical shells whose structure and dimensions obtain in modern hornless moving-coil loud-speakers.

Only a free-edge condition has been considered throughout the paper, since this agrees closely with the elastic suspension of a loud-speaker cone so far as the main vibrational modes, namely 2000 to 3500 ~, of the shell per se are concerned.

§ 2. THEORETICAL CONSIDERATIONS

The principal stresses involved in any form of shell are bending and extension, positive and negative. When the vibrations are associated mainly with one or other of these stresses, it is usually possible to determine the frequencies analytically. The analysis, however, becomes very formidable when both types of stress are of primary importance*.

So far as the bending of a shell of revolution is concerned, the frequencies depend directly upon the thickness and inversely upon the square of the radius, e.g. for the flexural modes of a cylindrical ring $f \propto ta^{-2}$, where t is the thickness and a the radius. If the governing stresses are tension and compression, the frequency is independent of the thickness but varies inversely as the radius, e.g. for the extensional modes of a cylindrical shell $f \propto a^{-1}$. f, t, a

It is clear that in an extremely thin conical shell the main factor is bending, the circumferential tension or hoop stress being of secondary importance. Consequently, if the radii and apical angle are constant, the frequency ultimately decreases with the thickness without limit. When the thickness exceeds a certain value, the circumferential stress becomes of comparative importance, and the frequency increases slowly with thickness to an upper limiting value—within the limitations of the case, since the thickness must always be finite.

For the thickness of paper and the apical angles used in the construction of loud-speaker diaphragms, there is both bending and circumferential stress, the latter being of considerable importance. Consequently, one would expect an expression for the frequency of vibration to be of the form $f \propto t^{n_1} a^{-n_2}$ where $n_1 < 1$ and $n_2 > 1$. n_1, n_2

In practice, however, there are three essential conditions which complicate the problem. Firstly, the radius of the driving-coil for any class of speaker is fixed; secondly, there is the mass of this coil; and thirdly, there is the former on which the coil is wound and the degree of stiffness it imposes at the minor radius of the cone. If the coil former is several times the thickness of the cone, the extensional deformation at the joint will be reduced appreciably.

In practice, therefore, we are concerned not merely with the case of a pure conical shell, which in itself appears to defy mathematical analysis, but with the more complicated structure due to the addition of a driving coil. In the experimental work described herein, the coil formers were of the same order of thickness as the paper

* Rayleigh, *Sound*, **1**, 395 (1894); E. Spenke, *Wissenschaftliche Veröffentlichungen Siemens-Konzern*, **10**, 128 (1931).

cones, so that considerable alteration of frequency would not be expected from this source. A greater source of disturbance is the mass of the coil, but its influence can be estimated by extrapolation.

These disturbing factors modify the values of the indices n_1 and n_2. Apart from the coil-mass etc., the influence of keeping the minor radius constant, instead of making it proportional to the major radius, is to make n_2 less than unity. As the major radius a is increased, the frequency decreases more slowly owing to the enhanced stiffness near the apex. The stiffness resides mainly in this region. This follows from the fact that the potential energy per unit mass of shell required to cause a definite deformation increases with decrease in radius.

If in a cone complete to the vertex it is *assumed* that the stress is purely circumferential*, the frequency varies inversely as the radius. This is easily proved as follows. Taking the vertex as the origin, the axis being coincident with that of y,

x, y let the radial extension be given by $\Delta x = \phi(y)$. Then the kinetic energy is

A_1, B_1 $A_1 \int_0^h \phi^2(y)\, y\, dy$ and the potential energy is $B_1 \int_0^h \frac{\phi^2(y)}{y}\, dy$ where A_1 and B_1 are con-

h, m stants and $h = ma$ = axial length of shell.

Thus the expression for the kinetic energy contains terms whose order in h and therefore in a exceeds that for the potential energy by two (a^2). Consequently, in finding f by equating the kinetic energy to the potential energy, the factor a must occur in the denominator.

If we take the first nodal circle to be $0{\cdot}8a$†, assume a deformation curve and proceed on these lines, we can obtain an expression for the frequency which gives values considerably in excess of those found by experiment.

For the thick‡ conical shells described herein, the vibrational frequency corresponding to one nodal circle *happens* to be given approximately by $f = \frac{m}{2\pi a}\sqrt{\left(\frac{E}{\rho}\right)}$

a, m where a is the major radius, $m = \cot \psi/2$, and ψ is the apical angle.

In other words, the frequency is nearly m times that of the purely radial mode of a cylindrical ring whose radius is equal to that at the base of the cone. As a case in point, take the glass cone of § 4, where

$$a = 12{\cdot}7 \text{ cm.}, \quad \psi = 107°, \quad m = 0{\cdot}74, \quad \sqrt{(E/\rho)} \doteq 5 \times 10^5 \text{ cm./sec.}$$

Thus $f = 4630 \sim$ whilst the experimental value is $4500 \sim$. In the case of a 90° aluminium cone of radius 19 cm., the values are $4260 \sim$ and $4400 \sim$ respectively§. In the latter case, the frequency of a cylinder having the same radius as the truncated end is $4260 \times 19/2{\cdot}5$ or $3{\cdot}24 \times 10^4 \sim$. If the vibration were purely radial, the frequency of the conical shell would obviously be much in excess of the observed value, owing to the large potential energy in the vicinity of the minor radius. Consequently, bending, etc. cannot be neglected.

* Actually this cannot exist alone since it implies additional stresses.

† Table 1, column 2; a = radius of base.

‡ For very thin shells the formula would not be so accurate.

§ The values of $\sqrt{(E/\rho)}$ have been taken from physical tables for both of the preceding calculations.

§ 3. EMPIRICAL FORMULA FOR VIBRATIONAL FREQUENCY

In a former paper* it was found that the main frequency of a series of 90° paper cones of varying major but constant minor radius and thickness, driven by a coil of mass 7·8 gm. was given by the expression $f = k_1 a^{-0\cdot67}$.

Starting with a very thin shell of constant radii, the frequency increases rapidly with the thickness at first, but ultimately settles down to an almost steady value. Over a certain range of thickness the frequency is given by $f = k_2 t^{0\cdot22}$.

If the action were one of pure bending, the index of t would be unity. The departure therefrom is caused mainly by circumferential stress, which in practical diaphragms is at least as important as bending. The index depends upon various factors such as coil mass, but it usually lies between 0·5 and 0·8 for cones used as loud-speaker diaphragms.

§ 4. SYMMETRICAL MODES OF VIBRATION

When an annular disc is driven quite symmetrically by a circular coil, the nodal figures corresponding to the centre-moving modes are concentric circles. With an annulus having inner and outer radii of 2·5 and 12·2 cm. respectively, the ratios of the first three modes are roughly 1 : 4 : 9, provided the mass of the driving coil is negligible. In a practical case the latter condition would only be realized approximately, the corresponding ratio being $1 : p : q$ where $p < 4$ and $q < 9$.

Owing to the different nature of the stresses in a disc and in a conical shell, the nodal ratios of the one bear no resemblance to those of the other. Accurate inferences cannot be made regarding these ratios from experiments on paper cones, owing to four pertinent factors: (i) heterogeneity, (ii) internal transmission loss, (iii) radiation loss, and (iv) low density of paper. By taking a heavy conical cast glass shade illuminating results can be obtained. Figure 1 (*a*) shows three resonances of an ordinary glass lampshade. These were obtained in a large highly damped room with a special microphone situated on the axis of the shade at a distance of about 180 cm. To avoid the influence of standing waves, the note supplied to the driving coil was varied $\pm$ 50 ~ continuously throughout the range of frequencies. The resonances were so sharp that the frequencies could readily be determined by ear, although actually the output curve was recorded. At each frequency the nodal figures were found and data relating thereto are given in the table.

Table. Data for glass cone.

Major radius a of shell = 12·7 cm., $\psi = 107°$, radius of driving coil = 2·5 cm., minor radius b = 1·4 cm., thickness $t \doteqdot 1\cdot65 \times 10^{-1}$ cm. Mass M_c of driving coil = 4 gm.

Nodal pattern	Radii of nodal circles	Frequency (~)
One circle	0·8*a*	4500
Two circles	0·6*a*, 0·92*a*	5700
Three circles	0·44*a*, 0·78*a*, 0·95*a*	7500

* *Phil. Mag.* **12**, 771 (1931).

Although nodal circles are specified, neither the drive nor the cone was sufficiently symmetrical or homogeneous to obtain perfect circles.

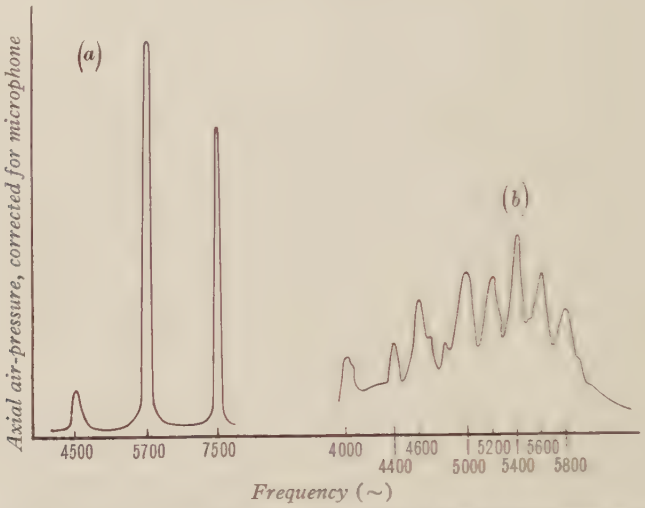

Fig. 1. (*a*) Axial air-pressure curve for free-edge conical glass shell corrected for microphone characteristic.

(*b*) Axial air-pressure curve for free-edge spun conical aluminium shell corrected for microphone characteristic. $a = 19$ cm., $b = 2{\cdot}5$ cm., $t = 4{\cdot}5 \times 10^{-2}$ cm., $\psi = 90°$, $M_c = 6$ gm.

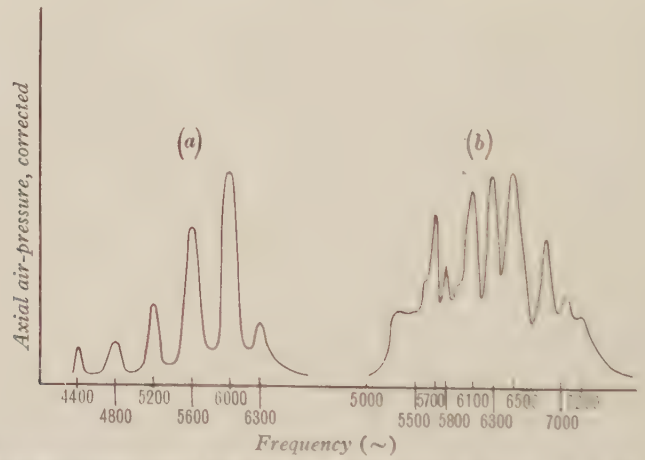

Fig. 2. (*a*) Axial air-pressure curve for free-edge spun conical aluminium shell as in figure 1 (*b*); but $t = 8 \times 10^{-2}$ cm.

(*b*) Axial air-pressure curve for free-edge conical aluminium shell with seam (seccotined). $a = 10{\cdot}9$ cm., $b = 2{\cdot}5$ cm., $t = 7{\cdot}5 \times 10^{-3}$ cm., $\psi = 90°$, $M_c = 1{\cdot}3$ gm.

Whereas the first mode is by far the most powerful with an annular disc*, it is the second mode which is the more powerful in the above case. There may have been

* *Phil. Mag.* 12, 115 (1932).

modes above 7500 ~, but the apparatus did not permit investigation beyond 9000 ~.

Experiments have also been conducted with aluminium cones, and some of the results are portrayed in figures 1 (*b*), 2 (*a*), (*b*). There are more than three peaks, but as the two thick aluminium cones were spun, whilst the thin one had a seam, the homogeneity cannot be expected to be as good as that of *annealed* cast glass. It should also be observed that here the second peak is by no means the maximum.

As a matter of interest and comparison, curve 1 of figure 3 shows the behaviour of a typical paper cone. The preliminary notch on the curve at 1800 ~ is an indication of the first mode. There are signs of others, whilst the main mode is fairly clearly

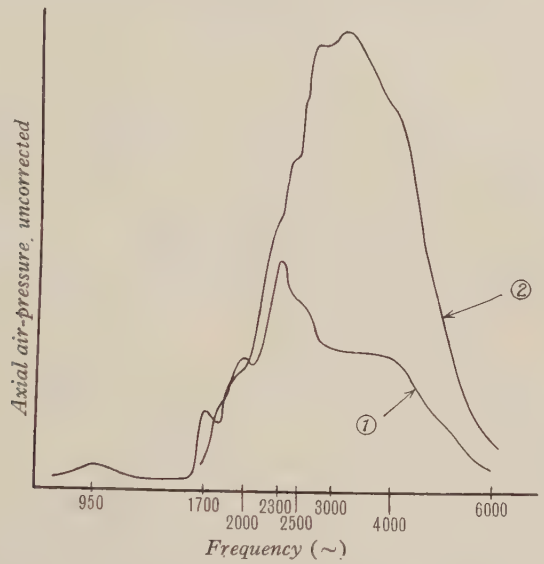

Fig. 3. Curve 1: Axial air-pressure curve for free-edge conical paper shell uncorrected for microphone characteristic.

$a = 12$ cm., $b = 2{\cdot}5$ cm., $t = 2{\cdot}1 \times 10^{-2}$ cm., $\psi = 90°$, $M_c = 7{\cdot}8$ gm.

Curve 2: as for curve 1, but $M_c = 2{\cdot}7$ gm. The reduced coil-mass results in increased and more uniform output above 2300 ~.

shown. But the modes of paper and aluminium do not stand out in the same conspicuous manner as those of the glass shade. This applies particularly in the case of paper when a light driving-coil is used.

The occurrence of the modes in cluster formation, as compared with the segregation that obtains in the case of a disc, is very striking. This is due to the different nature of the two vibrational systems. When the frequencies of the various modes cannot be definitely allocated, we shall refer to the frequency corresponding to the greatest output. At frequencies exceeding that of the main mode the output falls away, doubtless owing to losses.

§ 5. INFLUENCE OF THICKNESS OF SHELL ON ACOUSTIC-OUTPUT CURVE

When a curve delineating the acoustic output is taken on the axis of a coil-driven conical shell of given radii and apical angle, the profile depends upon the thickness and mass of the diaphragm. The general effect is clearly exhibited in figures 1, 2 and 3, which we shall now analyse. The curve for the thick heavy glass shade consists of three precipitous peaks separated by deep valleys. Owing to its great mass the general output-level is almost evanescent and it is only at resonant points, where the mass is offset by elasticity, that the output is readily audible. The thickest of the three aluminium shells shows the influence of considerable mass, but the valleys are shallower than those of the glass shade. Decrease in thickness is accompanied by a greater general output-level and the perceptible rising of the valleys towards the peaks. Finally, with a paper cone, especially when the mass of the driving-coil is small (figure 3, curve 2) the valleys and peaks coincide. Nothing is left to indicate the symmetrical modes except a boldly-rounded contour. The reduced coil and shell mass gives a greater amplitude between peaks, whilst the frictional damping and acoustic loading reduce the peaks. Although not fully understood hitherto, the combined influence of these factors has been invaluable in the construction of modern acoustic apparatus. And so empiricism has been justified.

§ 6. INFLUENCE OF COIL-MASS ON ACOUSTIC OUTPUT AND FREQUENCY OF VIBRATION

The mass of the coil affects (i) the mechanical impedance, (ii) the amplitude of vibration, (iii) the contour of the response curve, and (iv) the frequency of vibration.

ω Referring to the driving point, the mechanical impedance at a frequency $\omega/2\pi$ is B, M_e $B + j\omega M_e$ where B is the mechanical resistance and M_e the effective mass of the complete structure which may be positive, negative or zero. Since the coil can be considered as a rigid structure when vibrating axially, M_e can be written M_e', M_c $M_e = M_e' + M_c$, where M_e' refers to the shell and M_c to the coil. The value of M_e' is a small proportion of the natural mass in the nodal region*, so that the impedance is reduced appreciably when a coil of small mass is used. It follows that for any given driving force the amplitude of vibration and, therefore, the output increases. In fact, to preserve a good balance between the upper and lower registers, the mass of the coil must lie within prescribed limits. The latter are, of course, determined experimentally and depend to an extent upon the taste of the listener. If the mean frequency of the main nodal group is too low, the reproduction is woolly and lacks interpretational qualities. When it is too high we are wafted back to the juvenile days of playing tunes with paper and a comb. For any particular diaphragm there is a certain coil mass giving maximum output. The mass, however, varies with frequency owing to inconstancy of the diaphragm impedance†.

* *Proc. Phys. Soc.* **44**, 88 (1932).

† Letter to *Wireless Engineer*, p. 151, March 1932; *Proc. Phys. Soc., loc. cit.*

The profound influence of coil-mass on the contour of the axial pressure curve, and therefore upon the frequency characteristic, is displayed in figure 3. Whereas in curve 1 of figure 3, with a 7·8 gm. coil the notches and peaks are an indication of "modes," the same cannot be said of curve 2, where the coil-mass is 2·7 gm. The increased amplitude, sound-radiation and transmission loss concomitant with reduced mass-reactance culminates in a substantially uniform output-level over a certain frequency band. In fact, from an axial pressure viewpoint we have a good mechanical band-pass-filter effect.

So far as the influence of mass on the frequency of vibration is concerned, we cannot derive much inspiration from circular discs, since the vibrational conditions are dissimilar. One usually associates added mass with a reduction in frequency, especially when the mass does not contribute to the stiffness of the vibrator. Since

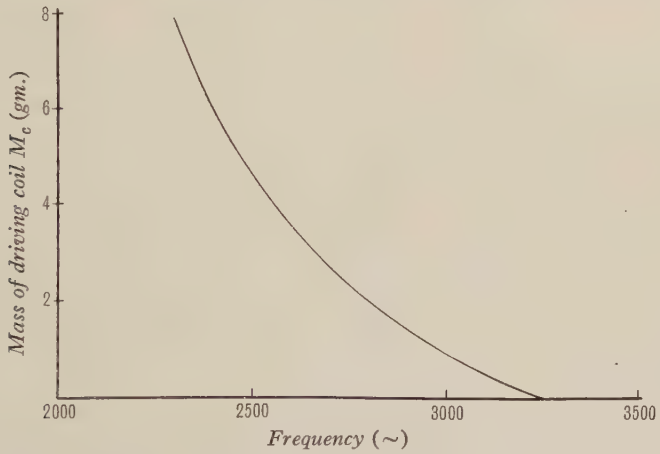

Fig. 4. Curve showing influence of coil-mass on frequency of main symmetrical mode of cone used for figure 3.

the modes of vibration are partly extensional, the influence of mass is less prominent than it would be under a bending regime.

To illustrate this feature a series of experiments was performed on a coil-driven shell, the frequency of the combination being determined for various coil-masses. Variation in mass was accomplished by the simple expedient of removing turns from the coil until a practical limit was reached. The results are plotted graphically in figure 4. By extending the curve until it intersects the horizontal axis, the frequency for a coil of zero mass is obtained. Owing to the stiffness imposed by the cylindrical paper former, this value may be on the high side. The frequency does not alter seriously with reduction in coil-mass until the latter is quite small.

In the ideal case of a lossless disc driven in vacuo where the coil does not contribute any stiffness, the influence of variations in coil-mass can be found by the simple expedient of shifting the frequency axis to the point where $M = M_c$, M_c being the coil-mass. Owing, however, to variation in acoustic loading and transmission loss with frequency, this artifice cannot be accurately applied to paper

cones. This will be evident from figure 3, which shows the influence of variation in coil-mass.

§7. INFLUENCE OF APICAL ANGLE ON FREQUENCY OF VIBRATION

The effect of the apical angle is exhibited graphically in figure 5. The rise in frequency with reduction in ψ is quite rapid from 180° to 100°. Beyond this the rise is curbed, whilst below 90° it falls away very slowly indeed. The general appearance of the air-pressure curves for various angles is shown in figures 3, 6, 7, where the resonances are in the neighbourhood of 2000 ~.

The relative power-output throughout the frequency range is not given by the ordinates of the axial air-pressure curves. This is due to (i) the microphone cha-

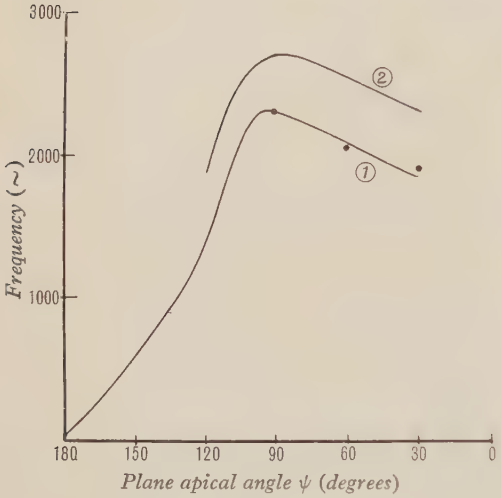

Fig. 5.

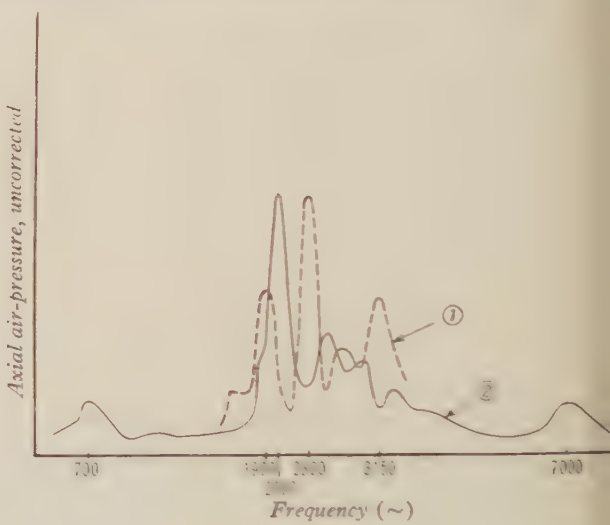

Fig. 6.

Fig. 5. Curves showing variations with apical angle in frequency of main mode.
$a = 12$ cm., $b = 2{\cdot}5$ cm., $t = 2{\cdot}1 \times 10^{-2}$ cm. Curve 1, $M_c = 7{\cdot}8$ gm. Curve 2, $M_c = 2{\cdot}7$ gm.

Fig. 6. Axial air-pressure curves, for free-edge conical paper shell with ψ equal to 60°, other dimensions as for figure 5, curve 1. Curve 1, with re-entrant cone 2·5 cm. in radius at apex. Curve 2, without re-entrant cone. The resonance at 700 ~ is due to the air column within the cone.

racteristic not being uniform; (ii) the current through the driving unit not being constant, since constant voltage was applied to the grid of the power valve; (iii) the spatial distribution of sound not being spherical*; (iv) variation in interference on the axis according to the number of nodal circles, i.e. the dynamic deformation curve of the shell. This is immaterial since the problem of the moment concerns the *frequencies* of vibration. In curve 2 of figure 3, where the frequency is indeterminate, an impulse method is used†.

* *Wireless World*, March 23, 30 and September 21 (1927); *Proc. R.S.* A, **122**, 604 (1929); *Phil. Mag.* **7**, 1026 (1929).

† *Wireless World*, April 3, 1929; *Phil. Mag.* **11**, 48 (1931); **12**, 140 (1932).

It has already been shown that when ψ is 90° the main frequency is clearly defined with a heavy coil, but loses definition when a light coil is used, figure 3. As the angle decreases, the definition is much improved, as will be seen from figure 6 for $\psi = 60°$. Two curves are given, one of which (curve 1) applies when there is a re-entrant cone at the minor radius. An auxiliary resonance is introduced at 1900 ~ and the main peak is shifted to 2300 ~. In curve 2 there is a series of minor resonances at 7000 ~.

The change caused by alteration in coil-mass is indicated in figure 7, where $\psi = 30°$. The main frequency is raised and the output enhanced, also the mode before the main peak becomes more prominent. The acuteness of the main peak

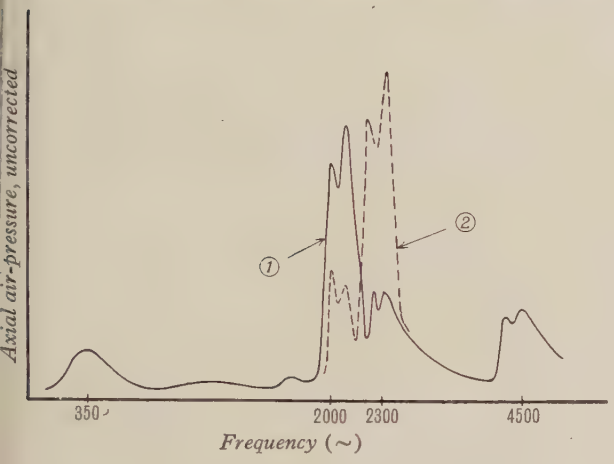

Fig. 7.

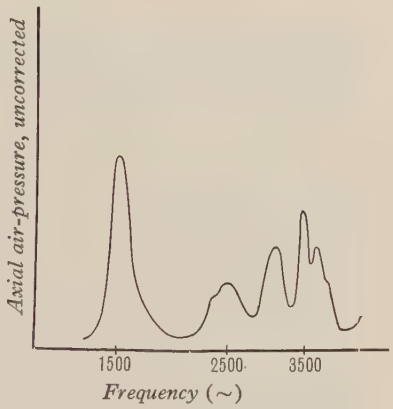

Fig. 8.

Fig. 7. Axial air-pressure curves for free-edge conical paper shell with ψ equal to 30° and other dimensions as figure 5, curve 1. Curve 1, $M_c = 4{\cdot}4$ gm. Curve 2, $M_c = 2{\cdot}7$ gm. The resonance at 350 ~ is due to the air column within the cone.

Fig. 8. Axial air-pressure curve of free-edge cylindrical paper shell. The output was very small and considerable amplification was required to obtain the record. Radius = 2·5 cm., $t = 2{\cdot}1 \times 10^{-2}$ cm. (with seccotined seam) length 56 cm. Driven by coil of 7·8 gm.

is in striking contrast with figure 3, where $\psi = 90°$. Moreover, a 90° cone is better suited for a loud-speaker than one of 30°. It is inferred that, owing to the small angularity of a 30° cone, bending is relatively of less importance and the transmission loss is reduced.

When the angle becomes appreciably greater than 90°, the main modes occur at too low a frequency to be of much value for loud-speaker work. This ought to be self-evident from figure 10, where $\psi = 135°$. It so happens, therefore, that for general reproduction an angle about mid-way between a disc and a cylinder gives the best results. I came to these conclusions regarding the angle ψ over seven years ago, entirely by aural observation. The scientific corroboration of one's sense of musical values is quite reassuring.

The slow change in frequency with reduction in ψ below 90° arouses curiosity regarding its ultimate value when ψ approaches zero and the axial length tends to

infinity. From the aspect of a nodal circle, the frequency ought also to be zero; but when a certain angle is reached, the cone becomes long enough for relatively important longitudinal vibrations to occur. It might be thought that the acoustic energy associated with such vibrations is very small. This is undoubtedly true, but the extension and compression of the shell give rise to an important auxiliary effect. By virtue of lateral expansion and contraction (Poisson's-ratio effect) portions of the cone vibrate radially and this augments the general output. Tests on a paper cylinder were made with the result given in figure 8. So far as could be ascertained by ear, a large portion of the sound was generated in this manner. Thus at a longitudinal node there is a radial antinode.

§ 8. AIR-COLUMN VIBRATIONS

In a letter to *Nature** the occurrence of resonances due to the air column in the shell was reported. An empirical formula for the main frequency is $f = c\ 2\ (l - ka)$,

c, l where c is the velocity of sound in free air, l the axial length of cone plus part of

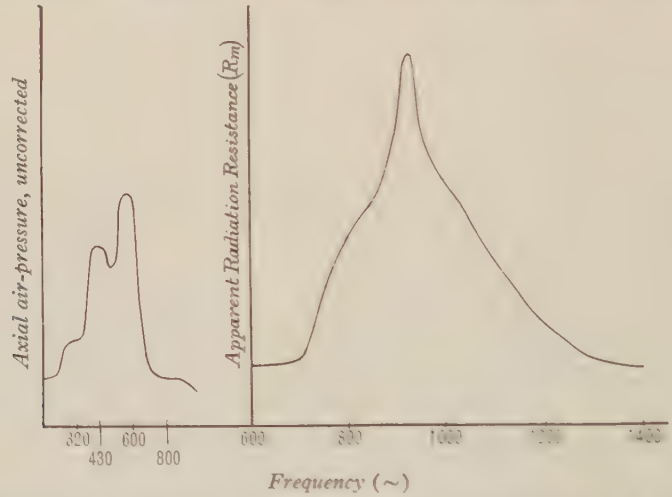

Fig. 9. (*a*) Axial air-pressure curve for cone of figure 1 (*b*) corresponding to air-column resonance band. The amplification required was considerably in excess of that for figure 1 (*b*) owing to the large mass of the cone.

(*b*) Apparent radiation resistance (*Rm*) for free-edge conical paper shell corresponding to air-column resonances. Dimensions as in figure 3, curve 1, but $M_c = 4{\cdot}7$ gm.

a, k coil former, a the major radius and k the end-correction coefficient, which varies between 0·6 and 0·8.

The form of the air-pressure curve in the vicinity of the resonance is of interest, and typical examples are given in figures 3, 6, 7, 9, and 10. In figure 10 the column resonances occur *above* the main nodal group, since ϕ is 135° and the air column short. A curve for a standard-size paper cone is portrayed in curve 2 of figure 9. The air-column resonance is then quite serious, being about 50 per cent of the

* February 6, 1932.

main nodal group which occurs just above 2000 ~. With heavy cones, e.g. of thick aluminium or glass, the amplitude of vibration is reduced considerably owing to large mass-reactance; and the column vibrations are of little importance in comparison with the symmetrical modes of the shell itself.

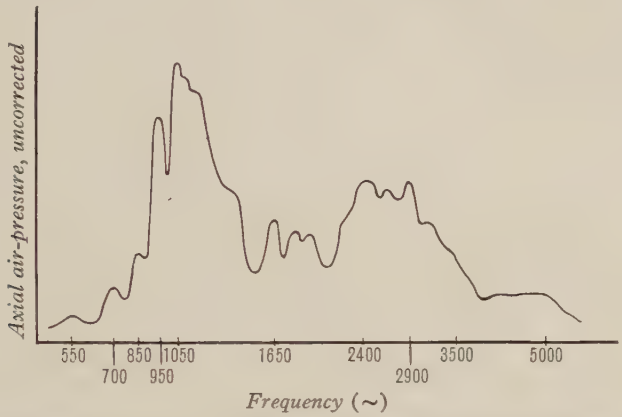

Fig. 10. Axial air-pressure curve for free-edge conical paper shell with ψ equal to 135°. The shell modes centre round 1000 ~, whilst the air-column resonances reside in the region of 2600 ~.
$a = 9{\cdot}5$ cm., $b = 2{\cdot}5$ cm., $t = 2{\cdot}1 \times 10^{-2}$ cm., $M_c = 2{\cdot}7$ gm.

§ 9. SUITABILITY OF VARIOUS MATERIALS FOR LOUD-SPEAKER DIAPHRAGMS

In a former paper* experiments with thin aluminium cones were described. Although quantitative measurements were not made at the time, it was shown that such cones were valueless as loud-speaker diaphragms. Figure 11 shows an

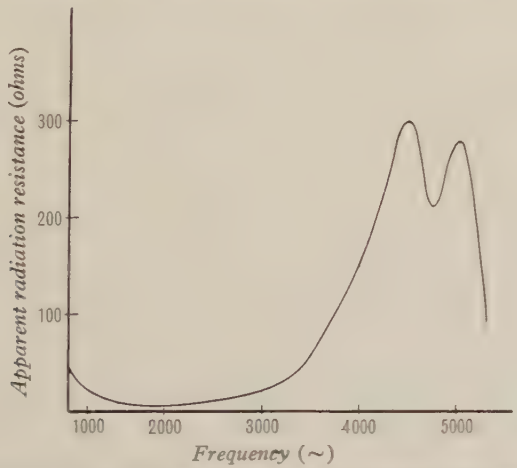

Fig. 11. Apparent radiation resistance (Rm) for elastically supported shell made from $7{\cdot}5 \cdot 10^{-3}$ cm. Aluminium sheet and having a seccotined seam*.
$a = 12$ cm., $b = 2{\cdot}5$ cm., $\psi = 90°$, $M_c = 4{\cdot}7$ gm.

* A report on the quality of broadcast reproduction with this diaphragm was given in *Phil. Mag.* **12**, 804 (1931).

output curve of one of the diaphragms where diaphragm loss is included. This curve is of a similar nature to that described from aural observation on broadcast reproduction.

The column resonances occur at about 800 to 900 ~, but the symmetrical modes lie between 4300 and 5300 ~. This is much too high a frequency and causes great aural irritation. Moreover, as was stated in § 8, for comfortable audition the main frequency group should lie between certain limits. This is accomplished by using a coil of suitable mass or some equivalent artifice. The output in the upper register must be properly proportioned to that at lower frequencies. In fact, a curve of the form shown recently in the *Philosophical Magazine** is desirable.

So far as the investigation has been pursued, such results have only been achieved by the use of paper of low density and suitable transmission loss. It is hardly necessary to state that glass shades and aluminium are quite beyond the pale, so far as the reproduction of speech and music is concerned.

DISCUSSION

Major W. S. Tucker. It is interesting to compare the cone employed as a transmitter with that employed as a receiver of sound. If the cone could be fitted with a stethoscope attachment, its responses to an external source of sound could be detected and the resonance peaks described in the paper could be found. The existence of these resonances in the walls of thin cones prevents their adoption for receivers in a binaural sound locator, where a sense of direction is derived by matching the phases of the received sound. The phase-distortion produced by resonance in the walls causes uncertainty if the cones are not perfectly matched. Hence in sound-locators, receivers with non-resonant walls are employed.

I am surprised by the author's view that the marked resonance shown in figure 10 for a paper cone of angle 135° in the region of 2600 ~ is attributable to the air-column. With a cone of such a wide angle one would expect resonances due to the air to be quite negligible.

Mr D. A. Oliver. This interesting paper raises a number of questions. I should like to ask why a warbling tone was used in a highly damped room when the receiver was only 180 cm. away from the source of sound, as standing-wave effects should then be very small. The physics of shell vibrations are preferably examined with a pure searching tone and it would probably be found that the peaks of figures 1 and 2 would then be higher and narrower. Among other factors, is it justifiable to neglect microphone corrections since, owing to cavity resonance alone, peaks as large as 3 : 1 above the general level can be obtained at about 3000 ~ with ordinary commercial condenser microphones; and if such a correction were necessary, the shapes of some of the curves (e.g. figures 3 and 10) would be considerably affected?

* *Phil. Mag.* **12**, 771 (1931), figure 9.

I have found that with paper cones, spun-metal coil-formers are better than paper formers, as the boundary condition at the cone-coil junction is then more definite. In § 4 it is said that the cast glass shade is expected to be more homogeneous than the spun aluminium cones. I should have thought that internal stresses in the glass would have reversed the order. Also from dynamical measurements which I have made of the velocity of sound in certain papers, I hardly think heterogeneity in the paper itself is a large factor, especially as the vibrations of a cone are not very dependent on small variations in thickness. In § 6 does Dr McLachlan mean that he would recommend increasing the mass of a light and satisfactory driving-coil to control the tonal balance? Would he agree that tonal balance is more efficiently obtained by using a light coil and making a suitable choice of cone angle, diameter and thickness?

I agree as to the general superiority of paper as a diaphragm-material—commercial practice is, of course, almost unanimous—but would add that celluloid and similar materials fall into an interesting class, having properties intermediate between paper and sheet-metal so far as density and internal damping are concerned.

Mr A. G. Warren. Some of the results which the author has obtained are particularly interesting in view of the inconsistent operation of loud-speaker diaphrams. Reproduction with a fair balance over the musical scale and with the resonances reasonably spread and not unduly exaggerated is possible, but unfortunately it is rarely obtained in practice. Resonances are essential; the difficulty arises in taming them without suppressing them. The behaviour of the paper diaphragm has been very puzzling. The author's method of approach has considerably clarified the problem. With annealed glass (which is reasonably isotropic) in a geometrically symmetrical form, the resonances are extremely sharp. The subsidiary resonances shown in the thin aluminium diaphragm figure 1 (*b*) are an interesting comment upon the known lack of isotropy in such material. Paper not only is anisotropic but varies in properties in any one direction. Further, geometrical irregularities are almost impossible to avoid. In consequence the resonances are much subdued.

It is interesting to note, in figure 11, scientific justification for one's natural dislike of the reproduction of the aluminium cone.

Mr G. A. V. Sowter. As the author points out at the beginning of this paper, the mathematical treatment of conical shells has been neglected. This is not unexpected in view of the great difficulty of devising analysis for such a complicated structure. Nevertheless, his experimental results enable him to give a complete explanation of the behaviour of the hornless loud-speaker. The good quality of reproduction obtainable from such a system, where resonances abound, was a mystery until Dr McLachlan's researches indicated the reason. It has been my pleasure to be associated with him in some of his work and I can confirm the accuracy of his conclusions regarding the various diaphragm-dimensions at which he arrived from a purely aural standpoint. A further proof lies in his design of the moving-coil loud-speaker which has been operating for some years (1926) in the

Science Museum. It is also interesting to observe, in connection with the thin aluminium cone mentioned, that the preliminary aural tests on broadcasting coincide very closely with the results to be expected from the curve of figure 11 measured subsequently. The performance of paper as a vibrational material is remarkable. Although measurements of Young's modulus sometimes reveal peculiarities, the main frequency with a given type of paper does not vary a great deal. This is rather striking, since paper cannot be regarded as homogeneous. With a paper cone the seam and the small undulations on the surface modify to some extent the acoustic output and generally broaden the frequency-response round the main resonance, which is all to the good. In curves taken by the author without a warble note, the profile over the resonant region resembled a small-tooth comb. Although the warble note smoothes out these serrations, the resulting curves are more easily interpreted, and the main effects, particularly with regard to frequency, are not masked in any way. The influence of the apical angle and the elastic modulus upon the output curves is very striking and shows what must not be done in loud-speaker design. The mass of the coil is an important factor, and in a number of commercial designs the powerful upper register is due to the radius of the diaphragm being too small and the coil too light.

Mr F. D. Smith. The author's measurements have been made at a point on the axes of the cones in a highly damped room. The method has many advantages in a study of the vibrational properties of cones; but, since the results are ultimately to be applied to the moving-coil loud-speaker, it needs perhaps to be supplemented by measurements in a moderately damped room at points off the axis. The use of a frequency of supply variable over $\pm$ 50 $\sim$ in combination with one or more microphones maintained in continuous motion should lead to a measure of the total energy emitted from the cone; supplementary measurements of reverberation time over the experimental range of frequency would further enhance the value of the results. It is interesting to note, in this connection, that a room can be designed to have a reverberation period constant to within about 20 per cent for all frequencies between about 40 $\sim$ and 10,000 $\sim$.

The lack of sufficient data relating to the current flowing in the moving coil in the various experiments and to the scale of the diagrams of axial air-pressure makes comparison of the diagrams difficult. Measurements of this kind can be placed on a more metrical basis by comparing the received e.m.f. from the microphone with an e.m.f. of known magnitude derived from the current flowing in the moving coil via a potentiometer, resistive attenuator, or mutual inductance.

It would be of interest to know the range of ψ over which the empirical formula in § 2 for the vibrational frequency of a conical shell is applicable. With reference to the table of data for a glass cone in § 4 it is noteworthy that the mode of vibration having one circular node produces relatively little axial air-pressure. Is this an indication of a small total output of sound-energy arising from a circulation of air between the two oppositely vibrating areas of the cone; or is there a cancellation by interference, at points on the axis, of the sound originating from these two vibrating

areas? When the spacing of antinodes on a cone, measured along the axis of the cone, happens to approach a regular series of half-wave-lengths, a relatively large axial pressure is to be expected. It seems possible to account for the largest peak at 6000 ~ in figure 2 (*a*) in this way. The effect on axial air-pressure of the mass of the moving coil is shown in figures 3 and 7. Were these curves taken with the same circuit density in the copper of the coils, or, in other words, is it legitimate to take the driving force as proportional to M_c?

Author's reply. I fully appreciate Dr Tucker's surprise regarding air-column resonances. The magnitude of this effect is exaggerated in figure 10 owing to focussing of the sound and to the rising characteristic of the microphone which is partly attributable to the same cause, cavity resonance. The air-column resonances in 90° paper cones are quite important as has been shown recently*.

Mr Oliver's remarks arise very largely from a misapprehension regarding the purpose of the experiments. I started with a pure tone, but was not absolutely satisfied that the results were always entirely free from standing waves. The object was to determine vibrational frequencies, not the power-output at such frequencies, and a warble note was employed. No fundamental resonances were missed. This was confirmed by bridge measurements of the resonances in figure 10. Incidentally this curve agreed well with that for a pure tone. So far as sharpness of definition is concerned Mr Oliver should surely be satisfied with figure 1 (*a*) unless he desires Shakespearean sharpness, "Keen as a razor's edge invisible." In certain cases with a pure tone a series of serrations was superposed on the main resonance band, which Mr Sowter compares to a small-tooth comb. This was probably due to local perturbations and general heterogeneity of the shell. Mr Oliver vetoes heterogeneity, but he cannot have it both ways. The majority of published acoustic measurements on loud-speakers are *axial* pressure curves with a plethora of paltry peaks. Analyses of these would be like looking for a particular proton in Persia—impossible! The warble note was employed to avoid this dilemma. Whilst I am on the subject of axial pressure curves, it is relevant to remark that owing to increase in focussing of the sound with frequency they are quite meaningless so far as sound-reproduction is concerned. An output or power curve is required. The curves in figures 1 and 2 are corrected for the microphone. There would have been little use in correcting all the curves, since the magnitude of a resonance depends on power output, not axial pressure. In any case I am not fond of hours of uninteresting arithmetic. A fair idea of the shape of the output curves can be gained from measurements of apparent radiation resistance†.

The results with paper formers depend upon the skill with which these are glued to the cone. I have never had difficulty so long as the apex of the cone was removed after the coil had been put into place. If Mr Oliver gets a close enough coupling between the coil and the metal former on which it is wound, the combination will

* *Nature, loc. cit.*

† *Phil. Mag.* **12**, 771 (1932).

simulate a transformer with short-circuited secondary. Then he will inaugurate an era of dumb and distortionless loud-speakers! I think he is under a misapprehension regarding the glass cone. The results indicate uniformity of structure, due to annealing as suggested by Mr Warren.

I feel sure that a number of commercial models would not be put on the market if their designers had any sense of musical values. Quality is a matter of personal taste and is not amenable to the laws of physics. Loud-speaker design is a compromise. If perfect reproduction could be obtained there would still be dissentients, so bizarre is the psychology of musical appreciation. So long as the public has an unsatiable appetite for jazz and the reception of foreign stations in the present congested state of the ether, high-class reproduction will not be a success. But that is no reason why we should not strive to improve loud-speaking apparatus.

The interesting contributions to the discussion by Messrs Warren and Sowter confirm my general views on the subject. This applies in particular to homogeneity. The velocity of propagation as found from $\sqrt{(E/\rho)}$ is not an acid test of homogeneity. If E and ρ each vary in proportion, $\sqrt{(E/\rho)}$ is constant, but it does not follow that the material is homogeneous. The fact that nodal figures on paper discs or conical shells are very irregular points clearly to heterogeneity*. Also the seam precludes any possibility of homogeneity.

Mr F. D. Smith will find quantitative measurements on the effect of coil mass in the October *Phil. Mag.* paper. In curve 3 of figure 12 of that paper, the resonance at 2000 ~ is due to a re-entrant cone. Without this auxiliary cone the main resonance occurs at 3000 ~†.

The scope of the formula in § 2 can be found by applying it to the data in this and other papers to which reference is made. Beyond this I have no experience. The small axial pressure with one nodal circle on the glass cone was due to reduced power. The increase in output with two nodal circles was very marked, whether one listened in the damped room or outside it down the corridor with the door open. Theory does not indicate the maxima and minima along the axis unless one is close to the diaphragm. The measurements were made beyond 180 cm. where such effects are absent. The increase in power above the first nodal circle is corroborated by measurements of motional resistance and this is clearly shown in the October *Phil. Mag.* paper.

The precise reason is rather elusive, but we can examine possibilities. Firstly the effective mass M_e is expected to vanish at a centre-moving mode. If for some reason M_e is not quite zero, the amplitude and therefore the output will be reduced. Secondly, although with one nodal circle the amplitude may be large, so also may be the interference in space due to the inner and outer portions of the shell vibrating in opposite phase. Ultimately the amplitude is curbed by transmission loss.

Figures 3 and 7 were obtained by applying constant voltage to the grid of the power valve, the output transformer being unaltered but the coil turns reduced.

* *Phil. Mag.* **12**, 115 (1932).

† See curve 1 in figure 6 of present paper.

The experiments were conducted some time ago and I cannot now guarantee that the amplifier-attenuator was unaltered. Consequently I should not like to advise Mr Smith to assume the force to be proportional to M_c.

My main object was to locate vibrational frequencies and to find the general influence of coil mass on the *profile* of the axial-pressure curve. The apparatus was at my disposal for a limited time during which it was only possible to do what has been described in the paper. I hope to publish analyses of the axial and spatial pressure-distribution and of the power radiated from flexible discs and conical shells in the near future.

PRESENTATION OF THE DUDDELL MEDAL FOR 1931

to CHARLES THOMSON REES WILSON, F.R.S.,

Jacksonian Professor of Natural Philosophy, Cambridge

Address by the President

PROF. C. T. R. WILSON'S contributions to physical science fall mainly into two groups: firstly those associated with the investigation of the tracks of ionizing particles, and secondly those associated with atmospheric electricity. But there is a connecting link between the two groups furnished by the word *cloud*.

I shall only deal very briefly with his work in atmospheric electricity. He has opened up new fields of inquiry along which great progress is being made. His method of studying rapid changes of the earth's electric field has led in his own hands and in those of others to a great increase in our knowledge of the electric fields associated with thunderstorms. By studying the changes of electric field at short distances from discharge channels, Wilson made the first trustworthy determination of the magnitude of the electric charge dissipated in a lightning flash. Appleton and Schonland working at greater distances confirm his view that thunderclouds are predominantly bipolar, the positive charge being elevated above the negative.

This work, together with Wormell's study of point-discharges in thunderstorm fields, gives the strongest support to Wilson's solution of what is perhaps the most important of all problems in atmospheric electricity, namely the maintenance of the earth's electric charge. The persistence of the earth's negative charge in fair-weather regions, notwithstanding the current of positive ions constantly flowing from the air to the ground, is attributed to the action of thunder and shower clouds, the charges of which are so disposed as to send negative electricity into the ground in sufficient quantity to balance the loss.

The other main line of Wilson's work branched off at a very early stage from his meteorological interests, but it was nevertheless his study of cloud-formation—the condensation of small drops of water out of supersaturated air—that led him to invent the expansion chamber, which is one of the most potent instruments of physical investigation ever devised. In his Nobel Lecture, delivered at Stockholm in December, 1927, when he received the Nobel Prize, he has told us how his attention was directed to condensation phenomena. During a short visit in September, 1894, to the Observatory which formerly stood on the summit of Ben Nevis, he became interested in the coronas and glories which the sun and clouds conspired to produce. Originally the optics of the phenomena engaged his attention; but when he set to work in 1895 to attempt the reproduction of the phenomena in the laboratory, the optics soon fell into the background and the investigation was

directed to the conditions of cloud-formation. He discovered that under certain conditions clouds could be formed in a supersaturated atmosphere free from dust particles; it had previously been supposed from Aitken's researches that dust was essential to provide nuclei for the drops to form round. Wilson found that there was a critical expansion ratio v_2/v_1, equal to 1·25, corresponding to 4-fold supersaturation; no drops were formed in dust-free air unless the expansion exceeded this limit, but when it was exceeded a shower of drops was seen to fall. The result was published in May, 1895. With more elaborate apparatus Wilson discovered a second critical expansion corresponding to 8-fold supersaturation. When this was exceeded dense clouds, consisting of very fine drops and associated with beautiful colour phenomena, were produced. Similar results were obtained with various pure gases.

The dense clouds due to the second critical expansion were explained by supposing that the gas molecules themselves acted as nuclei for the condensations, and interest became directed especially to the sparser shower formed at the first critical expansion.

The year 1895 of which I am speaking is the one which we usually name as the birth-year of the "new physics." Abroad Roentgen was discovering X-rays, the discovery being announced in the autumn. Close at hand J. J. Thomson was discovering the electron. Wilson was able to make use of a new X-ray tube made by Mr Everett in the Cavendish Laboratory. He found that when the moist air was exposed to X-rays, the first critical expansion, instead of producing a sparse shower of large drops, formed a dense fog consisting of very small drops which fell very slowly. In other words the action of X-rays greatly multiplied the number of the mysterious nuclei which operated at the first critical expansion.

The ionic character of these nuclei was next proved by their behaviour in an electrostatic field. Later study showed that it was the negative ions (i.e. the electrons) that gave the first condensation; for condensation on positive ions a 6-fold supersaturation was required.

In this way the whole phenomenon was disentangled. Owing to the large surface-energy involved, a drop cannot begin to form about nothing. If solid particles are lacking, the next most favourable nucleus is an electron. There are always a few of these present in a gas, due to various radiations including cosmic rays; but the number can be greatly increased by artificial methods of ionization. With higher expansion-ratios drops can be formed on positive ions or on molecules. Wilson now knew the proper conditions to bring each type of nucleus into operation. The next development was to use the line of drops to trace the track along which an ionizing ray or particle had passed.

We jump 15 years. Meanwhile many things had been discovered, including radium and its various radiations. Wilson, with his untiring pursuit of perfection, had spent infinite pains in making a suitable form of expansion apparatus and arranging efficient means of instantaneous illumination of the cloud particles for the purpose of photographing them. Whilst this was still incomplete it occurred to him to take a photograph with the rough apparatus already constructed to see

if he could detect with it the tracks of ionizing particles. In his Nobel Lecture he says:

"The first test was made with X-rays, and with little expectation of success; and in making an expansion of the proper magnitude for condensation on the ions while the air was exposed to the rays, I was delighted to see the cloud-chamber filled with little wisps and threads of clouds—the tracks of the electrons ejected by the action of the rays. The radium-tipped tongue of a spintharoscope was then placed inside the cloud-chamber, and the very beautiful sight of the clouds condensed along the tracks of the α-particles was seen for the first time."

His final improvement of the expansion method consisted in taking stereoscopic pictures, so as to enable the tracks to be plotted in three dimensions.

I will not attempt to enumerate the manifold results which have been obtained from the use of Wilson's cloud method of studying rays and particles. I will only say that broadly speaking the expansion chamber is to the atomic physicist what the telescope is to the astronomer. But it is perhaps appropriate to mention that at the moment we have chosen for honouring the inventor, all the expansion chambers in Cambridge (and probably throughout the world) are working overtime on a new discovery. The facts appear to be that *something* gets through a thickness of lead which no kind of matter hitherto known could penetrate, and on entering the expansion chamber buffets the atoms with momentum much too great to be carried by a quantum of radiation. Subject to further tests, some of which are now being made with Prof. Wilson's own apparatus, it is concluded that the invisible agent is a new element, *neutron*, of atomic number zero and therefore preceding hydrogen in the sequence of the elements.

Wilson is the man who first enabled us to see the atoms. By steps extending over nearly a century physics had been arriving at a theoretically conceived world of minute particles—a strange, almost incredible world, well-nigh transcending the imagination. Wilson made that world visible. With our own eyes we see the atoms deflected by a magnetic field; we see them collide, and verify that momentum is conserved. We see them disintegrate, an α-particle shooting off in one direction and the transmuted atom recoiling in the other direction. That is—provided we have an expansion chamber.

Do not be misled by those captious persons who will tell you that Prof. Wilson does not really show us the atoms but only remote indications of the atoms. Is there anything in Nature that we are aware of except by remote indication? If Wilson has never seen an atom, then I have never seen a star. I know that what he actually sees is a chain of little drops not in the least resembling a real atom, but from which an atom may be inferred. But it is the same with me; what I see is a system of diffraction rings not in the least resembling a real star, but from which a star may be inferred.

The amazing consequences which have sprung from Prof. Wilson's discovery, and the part which he himself has played in developing them, have tempted me away from the instrumental side of his work which is the primary ground of this award. I would like, however, to emphasize that his wonderful instrumental

technique, his perseverance and accuracy, and the standard of perfection which he set himself to reach, have been prime factors in his success. The following incident was related to me by an authority whose stories I do not always trust, but I am inclined to believe him in this instance. My informant who was going abroad went into Wilson's room in the Cavendish Laboratory to say good-bye and talk of various matters. Wilson at that time could not get his expansion chamber to work as well as he thought it should, and all the time they were talking Wilson had the plunger in his hand, grinding, grinding, grinding. Six weeks later the traveller returned and went to see Wilson again and talk to him of the latest scientific news. He found Wilson with the plunger in his hand, and all the time they were talking Wilson was grinding, grinding, grinding.

I do not know whether Prof. Wilson will confirm or deny this. If it should prove to be apocryphal, I may remind you that the character of a man may be revealed not only by the incidents which happened to him but by the stories which are told about him.

Nowadays, of course, expansion chambers are in use all over the world; and many of the foremost physicists have added their own skill and brains to obtain more results from Wilson's instrument. Nevertheless, it should be added that though he has many followers, for delicacy of work he is still unrivalled. The instruments elsewhere are no doubt adequate for most purposes; but I believe that if some point of special delicacy arises, nowhere in the world is there such perfection of technique as in the work of Wilson and his department.

I will end by quoting Lord Rutherford. When I told him of the duty I had to perform to-day, his words were "You cannot say too much about Wilson."

Prof. Wilson, in your expansion chamber we see some tracks that twist about, easily deflected. Others go straight as a die not to be turned aside by any obstacle in the path. I know of one physicist who resembles the latter. For 37 years your work has gone unwaveringly towards the goal of perfection at which you aim; and your determination has overcome all obstacles. I do not doubt that the portion of your track which is still ahead will afford further demonstration of your "penetrating power." It might seem inappropriate to wish a future of sunshine and fair weather to one whose delight is in clouds and thunderstorms. So, abandoning dangerous metaphor I ask you to accept this medal with our admiration and friendship; and may you have health and strength to bring further advance to our knowledge.

DEMONSTRATION

"Some lecture experiments." *Demonstrations given by* W. BENNETT, A.R.C.S., B.Sc., *on March* 4, 1932.

The electric bell. The insufficiency of the simple explanation of the action of the electric bell, as it is given in elementary text-books, is not always realized, though it is obvious when pointed out. Work is done on the armature only while it is moving toward the magnet with the contact made. The armature is drawn by the magnet and retarded by the contact spring. But it has to go back the same distance against what are at first sight the same forces. The action of the bell is made possible by the inductance of its windings, which delays the growth of the current when the contact is made and its decay when the contact is broken. Attention was called to this by M. Ch. Féry in May 1919* when he demonstrated before the French Physical Society an experiment similar to the one shown here. The present Lord Rayleigh has pointed out, however, that the explanation was given by his father no less than fifty-five years ago†. A bell of small inductance is made by removing as much copper and iron as possible from an ordinary bell. It will ring only when an iron core is introduced into a solenoid in series with the bell. Domestic-pattern bells which have been tested have inductances of 25 to 60 mH., and time-constants of 0·01 to 0·02 sec.

Fig. 1.

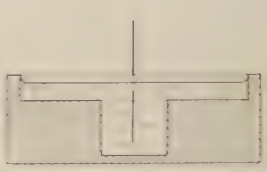

Fig. 2.

The electrostatic effect of a high-frequency current. The two leads of a galvanometer are joined together and taken to an insulated metal plate, standing vertically. One of the leads is cut, and a crystal rectifier is placed in it. A simple valve oscillator is set up at a distance of some feet, facing the metal plate. The galvanometer is deflected when the oscillator is working. The deflection increases with the frequency and with the amplitude of the oscillating voltage.

A simple magnetometer needle. A safety-razor blade is magnetized, floats on water, and carries two galvanometer mirrors attached, one below the blade and one above, to a light-stem passing through the centre of the blade. The water is contained in a shallow circular pit turned in the upper surface of a brass block. A central deepening accommodates the mirror, which is immersed. There is only a small clearance between the ends of the blade and the walls of the pit, and the blade keeps itself centred perfectly. The use of two mirrors in the same plane allows them to be set normal to the magnetic axis by the usual method of reversal.

* *Soc. Franç. de Phys. Procès Verbaux.*
† Rayleigh, *Sound*, **1**, 58 (1877); **1**, 68 (1894).

REVIEWS OF BOOKS

Recent Advances in Physics (*Non-atomic*), by Prof. F. H. Newman. Pp. x + 378. (London: J. and A. Churchill.) 15*s*.

Prof. Newman has had the courage to label his book as "non-atomic" physics, and the good sense to waive the implications of this sub-title whenever he has found it convenient to do so. The first two chapters are on the "Wave-like character of matter" and "Statistical mechanics" respectively. The remaining six correspond with the conventional subdivisions of classical physics—heat being represented mainly by an account of low-temperature work.

Although the style is clear, the book is adapted less to the needs of the general reader than to those of the young serious student of physics. To the latter, the scope of the work can be most easily conveyed in the statement that almost any one of the 112 sections of the book, taken at random, could form the nucleus of a discussion suitable for a physical colloquium. References are given to recent and very recent books and original papers; the bibliography has wisely been made representative rather than exhaustive, so that the reader is deprived of one excuse for not following up the references. The work should prove of much service to students reading for honours degrees, and possibly at times to their seniors. It will probably be of interest to physical chemists as well as to physicists.

H. R. R.

Smoke, A study of Aerial Disperse Systems, by R. Whytlaw-Gray, O.B.E., Ph.D., F.R.S., and H. S. Paterson, B.Sc. Pp. viii + 192. (London: E. Arnold and Co.) 14*s*.

This book, while doing full justice to earlier workers in the same field, is largely an account of long-continued and painstaking investigations carried out at Leeds. The authors have considered smoke "as a special type of disperse material and have tried to indicate how far the parallelism between aerial and aqueous suspensions implied in the term 'aerosol' really extends." This term, first put forward by Prof. Svedberg at the discussion on colloids in 1920, is indeed shown to be a picturesque label rather than a description justified by any real analogy. The comparative instability of smokes, the normal presence of particles with both positive and negative charges, and the general tendency to aggregation and chain-formation constitute profound differences between smokes and hydrosols. In an exhaustive discussion the authors find the cause of these differences in the nature of the dispersion medium, which, in comparison with water, has low viscosity and dielectric constant and contains a very small number of ions. The methods used in the investigation of sols accordingly require very considerable modification, and the procedures developed at Leeds are fully described in chapters on early investigations on smokes, errors in counting the particles in smokes, present methods of counting particles, the coagulation of smokes, and the determination of weight-concentration and size-distribution. Many of the methods described are of great ingenuity, like that of condensing water on the particles by adiabatic expansion, or the micro-filtration method of determining weight-concentration, and the chapters named will be read with profit by anyone interested in experimental technique.

The smokes investigated cover a wide range and include classical examples like ammonium chloride, smokes dispersed at low temperature (generally by "blowing a stream of dust-free and carefully filtered air at a known rate over the material heated in a metal boat") and smokes produced by making an arc between electrodes of the metal to be dispersed, and blowing a stream of air across the arc. A number of excellent photomicrographs illustrate the various types of particles occurring in these smokes; the oxide particles are particularly striking both for their markedly crystalline character and their tendency to aggregation.

A theory of coagulation is developed by introducing into Smoluchowski's deduction the modifications called for by a medium in which the mean free path is large compared with the dimensions of the particles, and the effects of polydispersity are fully discussed. The agreement with experimental results is as good as that found when Smoluchowski's original formula is tested for aqueous sols.

As regards the electrification of smoke particles, conditions are far more complicated than in hydrosols. In some smokes, such as ammonium chloride, all particles carry charges of the same sign, while in others, such as stearic acid, the numbers of positively and negatively charged particles are equal. In smokes dispersed at low temperature a high percentage of charged particles is present from the beginning and remains constant for some hours, while smokes dispersed at high temperature initially contain a small number of charged particles which rapidly increases with time.

While conditions are thus more complicated than in hydrosols, the possible explanations are more restricted, since the formation of such complexes as are postulated by Pauli and his school in all aqueous sols is ruled out. "If an aerosol is uncharged initially, it can only become electrified by catching ions from the air." The behaviour of a number of smokes is investigated experimentally and discussed from this one point of view.

It will be seen from this brief synopsis that the authors present (in very clear and simple language) a very complete survey of the properties of disperse systems in gaseous dispersion media, as far as they are known at present. They are quite aware that much remains to be done and devote to "Further problems" a final chapter which should stimulate further research. The book is a valuable contribution to our knowledge of disperse systems and will be welcomed by all who feel, with the present reviewer, that water is the most complicated of all dispersion media and that progress is to be achieved by getting away from it.

E. H.

The Donnan Equilibria and their application to chemical, physiological and technical processes, by T. R. Bolam, D.Sc., M.Sc. Pp. vii + 154. (London: G. Bell and Sons.) 9*s*.

It was a simple—almost innocently simple—observation that Donnan and Harris made some twenty years ago. Take an aqueous solution of congo red (the sodium salt of a complex sulphonic acid), dissolve sodium chloride in it and make an osmotic system by separating this solution from pure water by means of a parchment membrane. It will be found when equilibrium is attained that the concentration of the sodium chloride is greater on the water side than on the dye-stuff side of the membrane.

This modest beginning may be expanded into the general theorem that "the presence in any system of electrolytes of a species of ion which is restrained in *any* way from diffusing to all parts of the system will give rise to unequal distribution of every species of diffusible ion present. This *particular state of unequal ionic distribution* is the characteristic feature of Donnan equilibria."

Dr Bolam has built up the structure of the story extremely well and lucidly. His theoretical outline is specially good, beginning as it does with simple kinetic illustrations, and proceeding by nicely graduated stages through an elementary thermodynamical treatment to a general theory dealing with non-ideal solutions and taking account of activities. He then discusses some simple chemical illustrations, afterwards proceeding to physico-chemical, technical and biological applications. These last-named include an account of equilibria in the blood, and a very clear résumé of Duke-Elder's work on intra-ocular fluids.

The volume is compact in size, is well produced and forms a noteworthy contribution to the series of "Monographs on Modern Chemistry."

A. F.

The Physical Properties of the Soil, by BERNARD A. KEEN, D.Sc., F.Inst.P. Pp. vi + 380. (London: Longmans, Green and Co., Ltd.) 21*s*.

Millennia have slipped by since Adam digged outside the garden; but no systematic study of the soil appears to have been made until the work of G. Schübler was published at Leipzig in 1838. It is true that Fitzherbert's *Boke of Husbandry* had appeared in 1523 "dealing expressly with practical agriculture" and deserving "also to be remembered for the acuteness of many of the observations on soil cultivation. Fitzherbert possessed a keenly observant mind and his facts are given with surprising accuracy." Also an isolated *experiment* was made by J. Houghton (1681)—"important because it was the first recorded account of any attempt to classify soils on the basis of particle-size." "Not only did Houghton obtain a measure of the relative proportions of fine and coarse material in different soils, but he was able to observe differences in their properties from one soil to another." Small (a Scotsman) had experimented on, and Jefferson (third President of the United States, with an observant and mathematical mind) had thought out designs for, improved ploughs. These are mere incidents however compared with the work of Schübler, who studied apparent and real specific gravity, cohesion and plasticity, shrinkage on drying, moisture-holding capacity, evaporation and uptake of water, heat of wetting, specific heat, thermal conductivity, absorption of radiation, electrical conductivity and absorption of oxygen. He correlated the various properties with each other. Their names have been modernized but the subjects might have been taken out of a present-day volume on physical chemistry. The advanced character of these investigations can be in part realized by recalling that Ohm had published his electrical law only ten years previously and Joule had scarcely begun work on the conservation of energy.

The present volume is a lineal descendant of that of Schübler, but with all the advantages that are brought to it by the tremendous advances of physical science in the last century.

The soil is a composite thing, a loose aggregate of many components, whose function it is to bring food and water to the roots of plants. One of the main problems discussed is how to grade it and specify the properties required to carry out its functions. This is not a simple problem because soil is of so many kinds—fine clay, sand, pebbles and intermixtures of these. Houghton separated them by stirring the soil in water, allowing the mixture to settle, and collecting the sediment from time to time: the finest particles come down last in accordance with Stokes's law. Odén and Keen and others have sought to improve this process and have devised special balances for the purpose. Unfortunately any scale-pan immersed in the suspensions disturbs the fall, and these balance methods have had to be discarded owing to this inherent error (p. 66). The present mode employed internationally (though with minor national differences) is to pipette a sample from a given layer at depth x at the end of a given time t; this sample is assumed to contain no particles whose velocity of fall exceeds x/t; all particles with less velocity are present in the sample in the same concentration as in the original suspension. The bulk suspension is then thoroughly shaken and a fresh sample is taken corresponding to a different x/t and so on (p. 71). The method is not free from defect but it is the best devised so far, and international rules have been drawn up for carrying it out. In Switzerland and Czechoslovakia an exception is made in the preparation of the suspension. Small gravel is first separated out by sieving, but no attempt is made to disperse the remaining particles thoroughly; it is considered that the material should be left as nearly as possible in the state in which it is found in the ground (p. 76). Much can be said in favour of this contention; it leaves the finer particles cemented together (with lime, etc.) when they are so cemented in the ground. Fortunately the Odén-Keen balance can still be used for other problems (e.g. evaporation), though discarded as regards the purpose for which it was designed, and it is fully described (p. 82, etc.). Much work has been done on the way water distributes itself in such an assemblage of particles. The old method of replacing the

interstices between the particles by equivalent capillary tubes is far too crude to be of use. If water is contained in the interstices between spheres it may not be sufficient in amount to fill these interstices; the free surfaces of the water near each contact will then be determined by surface tension. Much of the work on this question has been elaborated at the Agricultural Station, Rothamsted.

The plasticity of soil and clay pastes has also led to fruitful experimentation (Chap. v). But more such work of a critical nature on well-defined systems is needed. It is interesting to learn that such work—as exemplified by the experiments shown at the recent Physical and Optical Societies' exhibition—is being conducted at Rothamsted. Much has also been done on the significance of the vapour-pressures above the soil (p. 212) and the information it may give concerning water-content. All the properties are being studied with a view to correlating to one another the biological and physical properties of soils. Another class of physical properties is concerned with dynamometer measurements of the resistance offered to the passage of cultivation implements. A full account of this work is to be found in Chap. VIII, while the succeeding chapters deal with soil temperature and atmosphere.

The volume gives a stimulating account of the work that is being carried out both at home and abroad. The term "soil" is given, however, to very varied materials, and in a climate like that of England it is subject to very varied circumstances; so that to the workers themselves the results obtained may sometimes give rise to disappointment. Nevertheless the subject is now in a totally different position from that which obtained at the beginning of the present century. We should have liked to have dealt with it more fully, and especially with the great contributions that have been made by British workers.

The book itself is well presented. It is fully illustrated with diagrams exhibiting the experimental results. There appear to be very few typographical errors. "Kirchhoff," p. 86, "W. Thomson (Kelvin)," p. 297 and "analytique," p. 307, should be spelt as here shown.

A. W. P.

Vision and Colour Vision, by R. A. Houstoun, M.A., D.Sc. Pp. viii + 238, 102 illustrations. (Longmans, Green and Co., 1932.) 15*s*. net.

A proper appreciation of the laws of vision, including those relating to colour, is becoming of much importance in various branches of industry and technology, and a book of moderate length giving a sound exposition of what is known on this subject would receive a warm welcome. Dr Houstoun is known among physicists as the author of papers on some aspects of vision, and the table of contents of his book suggests that it may well meet a real want. The chapters include discussions on the discrimination of intensity, dark-adaptation, acuity of vision, the visibility of the spectrum, the laws of colour-mixing, theories of vision and colour-blindness, and many other not less interesting topics. The first chapter is entitled "Units" and begins

"Light can be measured in three kinds of unit...the erg...the metre-candle...the brightness unit. This unit is wholly subjective and has hitherto found very little use. It is one of the functions of this book to develop it. The possibility of a brightness unit has been denied in some quarters. As much of the confusion at present existing in colour-vision theory arises from the fact that observers have not attempted to give numerical values to their sensations, we shall proceed to elucidate...."

After so direct a challenge to his views the more or less orthodox physicist anticipates a discussion in which accurate experiment and observation, combined with forcible logic, will compel him at least to reconsider and possibly to modify some of his views.

This expectation is not realized: the book in fact is very disappointing. Dr Houstoun has clearly read widely in the subject, and this book is largely composed of extracts from and comments on his readings, together with a description of experimental work he has

carried out either alone or in collaboration with others. A reader can hardly escape from the conclusion that the author has at times failed to grasp the real significance of what he has read. Many of the chapters are by no means satisfactory. The text often requires correction; at times the meaning is obscure, and examples of direct contradictions in different passages are not wanting. The author exhibits a weakness for introducing (sometimes on very doubtful evidence) speculations which apparently lead nowhere, and in at least one place he leads an argument in a particular direction with an "undoubtedly" when there is a complete lack of evidence whether that way or another is correct. Many of the experimental conclusions he accepts appear to the reviewer not to have been established owing to the neglect of important conditions. In general the work suffers from an insufficiently critical attitude on the part of the author.

Detailed criticism of the bulk of the book is unnecessary. It will suffice to comment briefly on the last chapter, to which some of the earlier parts lead up. This chapter is entitled "The theory of colour-vision," by which we are to understand the theory Dr Houstoun advocates—other theories have been mentioned in an earlier chapter. In the opening section, entitled "The argument against the Young-Helmholtz theory," it is claimed that this theory (i) violates common sense and (ii) leads inevitably to mathematical contradictions. Objection (i) is unsubstantial, and it is sufficient here to say that the criticism applies equally to Dr Houstoun's own theory. On (ii) the author says "I have known for years that the Young-Helmholtz theory was mathematically untenable, but did not arrive at the above proof until two years ago." In this "proof" an essential part is played by the measures of sensation. Had Dr Houstoun looked back to the opening section of his book he would have been reminded that many—certainly a large number of adherents of the Young-Helmholtz theory—do not admit numerical scales of sensation. Thus the proof, if otherwise valid, would not have been relevant to the Young-Helmholtz theory: it can only apply to a theory, such as Dr Houstoun's, which incorporates measures of sensations not linearly related to the measures of the stimuli which evoke them. If the argument of this "proof" is examined it will be seen that it rests upon the *assumption* $2S(x) = S(2x)$, where $S(x)$ is the measure of the sensation resulting from the stimulus measured by x. The author has put his statement in such a way that he has failed to see what he has assumed, and by including unessential colour terms has deceived himself into believing that it is of significance to the theory he is attacking. He has, in fact, completely failed to establish the existence of any inconsistency in the Young-Helmholtz theory.

It is clear that in the reviewer's opinion the book is not to be recommended to those who are setting out to learn the fundamentals of vision and colour vision. Those who already have a good knowledge of these subjects will not necessarily find its perusal unprofitable; their views are likely now and then to differ enough from the author's for the conflict to be stimulating, and they may be led to realize more fully the outstanding importance to the progress of this science of precise measurements of indisputable significance. For example, our knowledge of colour-blindness would be immeasurably advanced if investigations comparable with those carried out in recent years on normal subjects were to be undertaken on a few selected persons.

In conclusion attention may be called to a small error which is repeated often enough to irritate—the use of the contraction $\mu\mu$ where $m\mu$ is meant. T. S.

Mathematical Tables, Vol. 1, by The British Association Committee for the Calculation of Mathematical Tables. Edited by J. Henderson. Pp. xxxvi + 72. (London: British Association.) 10*s*.

The books of tables to which we are most accustomed give the values of functions to not more than 7 figures, and interpolation is by proportional parts; but when a table is first calculated, things are quite different. Briggs's *Arithmetica* (1624) and Vlacq's so-

called *Editio secunda* (1628) gave logarithms to 14 and to 10 figures respectively, whilst Rheticus (1596) calculated sines every 10″ to 10 decimals, and extended the accuracy to 15 places years later. Nearer to our own day we find Glaisher tabulating $1\ x!$ to 28 significant figures, Hayashi giving its square to 23 figures, and Stieltjes giving the sum of the series $\sum_1^\infty r^{-x}$ to 32 figures for every integral value of x from 2 to 70. Manifestly the entries in such tables cannot be separately calculated at sufficiently close intervals of the argument to make linear interpolation possible, and they are only regarded as the basis of other, more convenient, tables. Normally the high-accuracy table now finds its home in one of the mathematical journals, and is only consulted on the rare occasions when it is imperative to employ such accuracy—chiefly for the calculation of tables of some other function.

The British Association Committee which has been sitting since 1873 (but not with the same personnel throughout) to deal with the subject of mathematical tables has now broken somewhat fresh ground by collecting together all the tables save those of Bessel functions and those connected with the theory of numbers which have been published in its reports. The tables have been re-arranged, since their first publication, so as to present them in a form suitable for use with Everett's interpolation formula and, to assist in this, the differences of even order are tabulated also.

Of the functions given, we single out firstly the sines and cosines up to 50 radians, at every tenth of a radian, together with a table up to 1·6 radians at every thousandth of a radian. Of these, the first table is given to 15 figures, and is only of use at the arguments actually tabulated. It cannot be interpolated to its full accuracy. The other table goes to 11 figures, and may, with the assistance of the table given for $n = 2$, be used to obtain the sine and cosine of any angle. The introduction to the tables mentions that a 23-figure table calculated by Van Orstrand is available, and it may be useful to mention that there is also one to 21 figures, using the sexagesimal division of the degree in *Abh. Berlin* for 1911. It was computed by Peters.

Next, there are tables of $\sinh x$ and $\cosh x$, as also of $\sinh \pi x$ and $\cosh \pi x$, all to 15-figure accuracy, and of the functions

$$\int_0^x \sin x\,dx/x, \quad \int_\infty^x \cos x\,dx/x \quad \text{and} \quad \int_{-\infty}^{-x} e^{-x}\,dx/x.$$

These will all be of great help, since none of them has a competitor in respect of both range of the argument and accuracy. Incidentally, the introduction implies that the Committee have not been aware of the table given by Miller and Rosebrugh in *Trans. R.S. Canada* (1903) where $Ei(x)$ is given from 0·1 to 2, with 9-figure accuracy.

The gamma function, which is here called the "factorial function," is tabulated with 12-figure accuracy from 0 to 1 at intervals of 0·01; a table of this range (with a table of factorials), of course supplies the value for any argument. In addition to this are tabulated the integral of $\log \Gamma(x+1)$ and its first, second, third and fourth derivatives, which may also be written as the sums from $r = 1$ to $r = \infty$ of certain convergent series, the typical terms being $x/r(r+x)$, $(r+x)^{-2}$, $2(r+x)^{-3}$ and $6(r+x)^{-4}$ for the four derivatives in order. Similar series with x equal to 1 are also tabulated in the introduction, viz. $\sum_{r=1}^\infty (1+r)^{-p}$ for all values of p from 2 to 35, the results being given to 16 decimal places. This table is regarded as subsidiary, and is not quoted in the list of contents. In connexion with this set of functions, it should be realized that although Emde's 3-figure table from $x = 0$ to $x = 1$ is not a substitute for the fine table here given, yet it suffices to nullify the claim in the introduction that only one table had been given previously. Actually, Emde's appears to have been the earliest, since it was published in 1906, and Miss Pairman's in 1919.

A word as to the terminology employed may not be out of place. The gamma function

is called the "factorial function," presumably in view of the fact that $\Gamma(x+1) = x\,\Gamma(x)$, so that x is a factor of the function. The change seems to have much in its favour but, if it is to be adopted, let us at least be consistent. In these tables, the derivatives are styled the "polygamma functions" (the 1st derivative is digamma, the 2nd trigamma, and so on) which seems to be pointless if the primary function is not the gamma function.

The last group of tables gives a set of functions which have so far been studied only by the mathematical statistician but will certainly find their way into general mathematics sooner or later. They are here called the Hh_n functions, where n is an integer. Hh_{-1} is $e^{-\frac{1}{2}x^2}$, and the others are such that $Hh_{n-1} = -d(Hh_n)/dx$. Consequently those with negative n are, save for a factor $e^{\frac{1}{2}x^2}$, the Hermite polynomials which have recently become interesting to the student of wave mechanics. Another member of this set of functions, viz. $Hh_0(x)$, gives in effect a table of the error function, since $erf(y) = 1 - (2/\pi)^{\frac{1}{2}} Hh_0(y\sqrt{2})$. In this particular group of tables, interpolation is naturally by Taylor's series, because the functions of the successive orders supply the terms $f(x), f'(x), f''(x), \ldots$ required in that series.

The volume is extremely well produced, and the paper and type are good, whilst the price is distinctly low. A great deal of tedious labour must have been expended on the production, but this will be repaid in the gratitude of the users, for it cannot be denied that a single volume of tables of quarto size is vastly more convenient than the whole shelf full of B.A. reports which it renders superfluous. And anyway, we do not all possess copies of the reports for our very own, even if we should like to!

J. H. A.

Tables Annuelles de Constantes et Données Numériques, Vol. **8**, 1927–8. Pp. xl + 1101. (Paris: Gauthier Villars et Cie.)

Prof. Marie's magnificent publication pursues its majestic course. The present volume contains data for the years 1927–28, and covers the usual ground—elasticity, viscosity, density, surface tension, expansion, specific heats, thermal conductivity and other topics, heat, acoustics, electricity and magnetism, radioactivity and certain branches of optical science, including emission spectra, are represented in this volume. The limits of selection are very wide indeed, and it would be difficult to find a relevant experimental paper of any value which has been overlooked. The volume is indispensable and is destined to be used heavily; that being so, it is unfortunate that it should be covered only, and not properly bound.

A. F.

Proceedings of the Institution of Mechanical Engineers, Vol. **120**, January to June, 1931. Pp. viii + 781. (London: Institution of Mechanical Engineers.)

The present volume contains a number of papers which deal with some important developments in modern engineering. The paper by Mr H. N. Gresley on high-pressure locomotives gives an account of the first high-pressure locomotive to be built in this country. In this there is a water-tube boiler of the Yarrow type, a completely new departure from the fire-tube boiler which has now been in use for a hundred years. In accordance with developments in other modern steam plant the object has been to generate steam at much higher pressures. In Mr Gresley's locomotive the boiler pressure is 450 lb./in.^{2}, but he describes another locomotive working on the German State Railways under a pressure of 1700 lb./in.^{2}

Messrs R. S. Allen and W. E. W. Millington have contributed an interesting paper on modern methods of raising water from underground sources. Here the centrifugal pump has been applied to the pumping of water through a bore-hole as deep as 300 ft. The pump, which runs at 1000 r.p.m., is placed in the bore-hole and is connected to the

motor at the surface by a long vertical shaft. In this connexion considerable mechanical difficulties have been surmounted, and the paper is a tribute to the skill of the engineer.

In his paper on post-war land-turbine development Mr C. D. Gibb reveals some interesting facts relating to the modern steam turbine. Here, as in the locomotive, one is impressed with the use of steam-pressures over 1000 lb./in.^{2} But probably the most important development is in the construction of the blades. Blade speeds have now been increased from 600 ft./sec. to 1200 ft./sec., and blades are being made as long as 34 in.

There are three papers devoted to the internal-combustion engine, of these the paper by Messrs Farmer and Alcock on fuel injection systems for high-speed oil engines is perhaps the most important. In this, airless injection systems are dealt with, and in particular an analysis of the mechanics of the timed-pump fuel-injection system is given. Diagrams derived from the theory developed are shown to agree reasonably well with diagrams obtained by the authors from engine tests. The paper is an important contribution to knowledge of a rather specialized character relating to the high-speed oil engine.

The fatigue of metals is dealt with in another three papers; these record the results of much work on the failure of spring steel by fatigue. Two of the papers relate to helical springs and the third to laminated springs, and the importance of the effects of surface conditions of the materials on resistance to fatigue is shown clearly in one of these papers.

Prof. Coker gives another contribution to his work on photo-elasticity, and this with some other shorter papers make up a very large but important volume of the *Proceedings*.

G. A. W.

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